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The descriptions are divided into five categories: pyrometallurgical processes, hydrometallurgical processes, electrolytic processes, air pollution control processes, and water pollution control processes. If data were available, each process description includes a discussion of economic, environmental, and energy considerations, as well as a discussion of the basic operating principles. A detailed analysis of each process is not attempted in this report. For additional information, the reader is referred to the list of references and bioliography following each process description.

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OVERVIEW OF FOREIGN NONFERROUS SMELTER TECHNOLOGY

by

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Contract No. 68-03-2577

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report presents a brief overview of numerous production and pollution control processes that are in use or under development abroad for the production of nonferrous metals. This report is not intended to imply that any specific technique is applicable to domestic practice, but rather to inform the reader of new technological developments so that he may pursue those items of interest. For additional information, the reader is referred to the bibliographies following each process description.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Numerous production and pollution control processes that are not used in the United States are in use or under development by foreign nonferrous metal producers. Although some do not apply to U.S. conditions, others can reduce pollution, increase production, or lower costs. Many of these foreign processes are described in this report.

The descriptions are divided into five categories: pyrometallurgical processes, hydrometallurgical processes, electrolytic processes, air pollution control processes, and water pollution control processes. If data were available, each process description includes a discussion of economic, environmental, and energy considerations, as well as a discussion of the basic operating principles. A detailed analysis of each process is not attempted in this report. For additional information, the reader is referred to the list of references and bibliography following each process description.

Data for this report were obtained from foreign and domestic journal articles, patents, books, symposium proceedings, and industry literature. Technology in the copper, lead, and zinc industries is emphasized.

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Project officer for the Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency was Mr. John O. Burckle.

The authors appreciate the efforts and cooperation of everyone who participated in the preparation of this report.

SECTION 1

INTRODUCTION

This report is an overview of foreign nonferrous metallurgical and pollution control processes not used in the United States on a commercial or pilot scale. Information on the status and operating principles of these processes was obtained from available literature.

Although emerging technology is stressed, not all processes described represent the latest developments in nonferrous metallurgy; some are older techniques that may not be readily applicable to conditions in the United States (e.g., Imperial Smelting is not applicable to most U.S. ores). Emphasis, however, is placed on metallurgical and pollution control techniques that have been demonstrated on at least a pilot scale and may be of use to the U.S. copper, lead, and zinc industries. The energy consumption and environmental effects of a process are addressed when possible.

For the convenience of readers interested in obtaining additional information about the processes, references are given by subsection. When appropriate, a bibliography is also included at the end of each description.

A special system of referencing is used in this report. One or more reference numbers directly after a subsection title indicate that all the material in the subsection is drawn from the reference(s) cited. A reference number after a sentence within a paragraph signifies that only the information in that sentence comes from the reference cited. One or more references after the last sentence of a paragraph show that all the information in the paragraph is based on the reference(s) cited.

SECTION 2

PYROMETALLURGICAL PROCESSES

2.1 MITSUBISHI PROCESS

In 1961, Mitsubishi Metals Corporation set out to develop a process of continuous, pollution-free copper smelting. After pilot-scale operations at the Onahama smelter proved the technical feasibility of the process, Mitsubishi built a commercial-scale plant with a capacity of 48,000 Mg/yr of blister copper at the Naoshima smelter. A second commercial-scale plant is under construction by Texas Gulf at Timmins in Ontario, Canada. The capacity of the Canadian plant is projected to be 59,000 Mg/yr, and later to be expanded to 118,000 Mg/yr.[1-4]

As shown in Figure 1, the Mitsubishi process is composed of three metallurgical stages, each of which is carried out in a separate furnace. Concentrates are smelted in the first, slag is cleaned in the second, and matte is converted to blister copper in the third.[5] Intermediate products in the molten state move continuously between the furnaces.

Raw materials are charged through the top of the smelting furnace by vertically installed lances. Use of lances for charging and blowing increases rates of smelting and oxidation and simplifies design and maintenance. Top blowing offers the advantage of introducing oxygen or fuel oil through the lances when necessary.

Matte and slag produced in the smelting unit continuously flow to the slag cleaning furnace as an emulsion. Cleaned slag is skimmed continuously and granulated, and the matte is

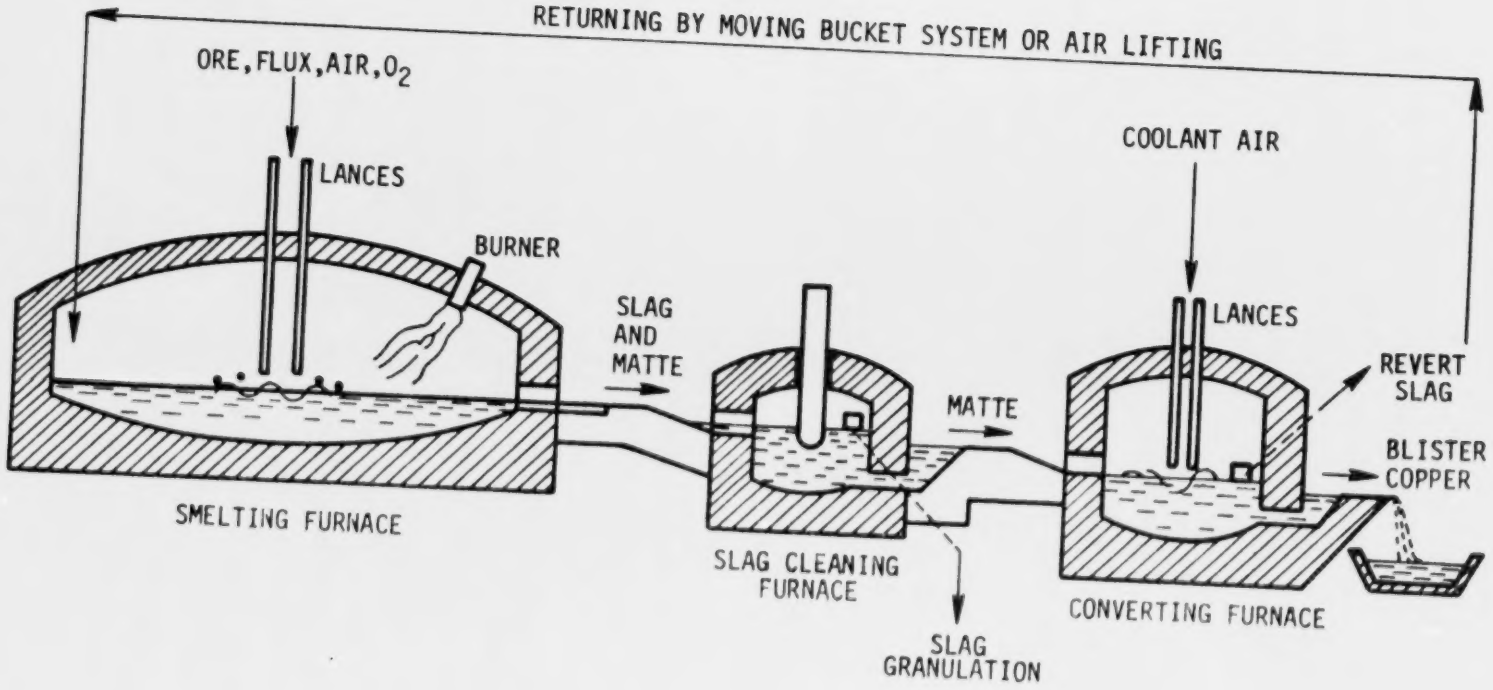

Figure 1. Schematic view of the Mitsubishi semicommercial process.[5]

sent to the converting furnace. Average copper loss in this waste slag is about 0.4 percent.

With lances that introduce blow air, the converting furnace oxidizes the matte to blister copper, which is continuously tapped from the furnace. Slag formed during the converting stage is recycled to the smelting furnace by a moving bucket system.

The average sulfur dioxide (SO_2) content of the combined off-gases from the three furnaces is greater than 10 percent. When the smelting furnace is operated with 25 percent oxygen-enriched air, SO_2 concentration is fairly constant and permits economic recovery of sulfur as sulfuric acid or elemental sulfur.[6] Dusts generated by the system can be collected and treated for minor element recovery by conventional techniques before recycle to the smelting unit.[7]

The Mitsubishi process should not significantly harm water quality. A settling pond is not needed because slag is treated in an electric furnace. As with conventional smelting, granulated slag is disposed of easily; depending on local markets, it may be used for cement manufacture or road beds.

A plant using the Mitsubishi process is estimated to require only 70 to 80 percent of the capital investment needed to build a conventional smelter. This low capital investment is attributed to relatively simple engineering design involving the continuous gravity flow of molten intermediate and final products and to higher output per volume of smelting unit because of an increased smelting rate compared to reverberatory smelters.

The Mitsubishi process requires only 2.7×10^6 kcal/Mg to produce a product, whereas conventional smelting requires 5.2×10^6 kcal/Mg.[8] This low fuel requirement is attributable to the compactness of the furnace and the maximum use of the reaction heat of the iron and sulfur content in concentrates by the production of high-grade matte in the smelting furnace.[7]

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2.2 BRITCOSMACO PROCESS[1]

The Britcosmaco process, developed in Australia by consulting engineer G.F. Brittingham, is intended to combine the best features currently available in pyrometallurgical treatment of sulfide ore concentrates. As shown in Figure 2, dry concentrate and flux are fed into the main smelting shaft with sufficient preheated or oxygen-enriched air for autogenous smelting. An enriched white metal and a slag are produced and collect on the hearth in two layers.

The slag increases in volume and flows along the phase reaction section of the hearth; contact with low-grade matte causes more copper to be rejected. As the slag flows toward the tap hole, it is reduced to a greater extent immediately under the secondary smelting shaft. Between the shaft and the tap hole, fine particles of matte disperse through the slag and reduce the oxygen potential even further, causing additional rejection of copper.

As it falls down the main shaft, copper is oxidized and works through the slag layer. It dissolves at the top of the enriched metal layer and precipitates from the bottom as metal. The copper is removed by a bottom tapping siphon.

According to Brittingham, the Britcosmaco process is advantageous because copper recovery is higher than for conventional

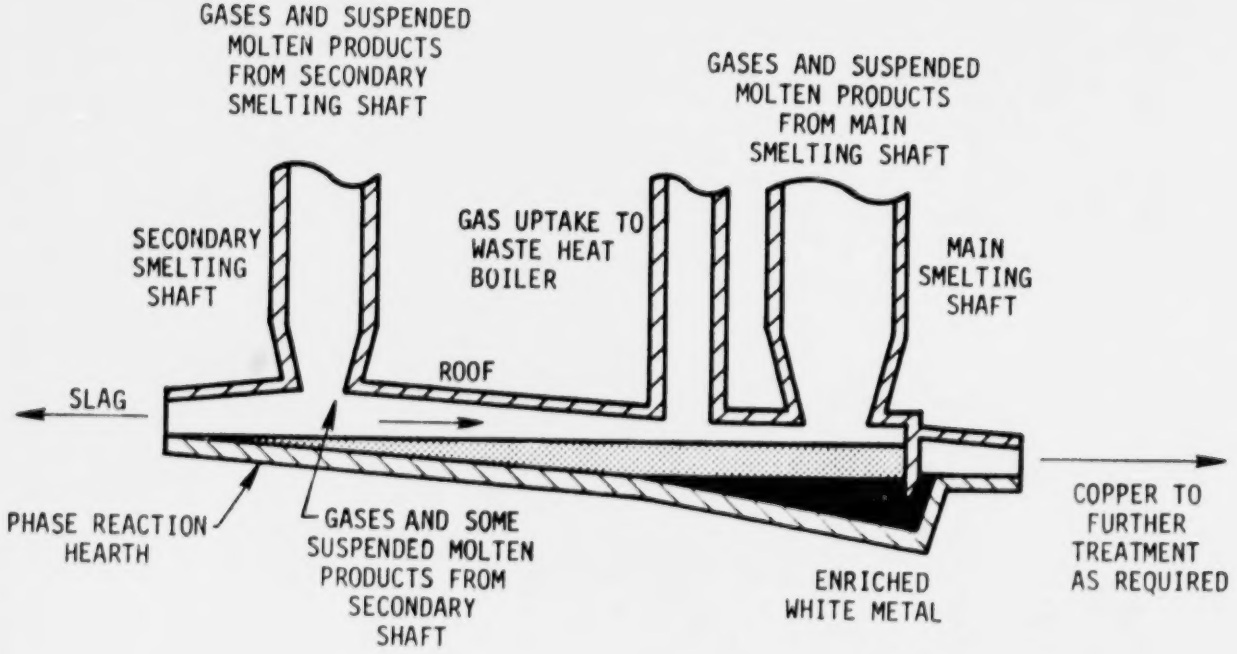
GASES AND SUSPENDED MOLTEN PRODUCTS FROM SECONDARY SMELTING SHAFT
GASES AND SUSPENDED MOLTEN PRODUCTS FROM MAIN SMELTING SHAFT
SECONDARY SMELTING SHAFT
GAS UPTAKE TO WASTE HEAT BOILER
MAIN SMELTING SHAFT
ROOF
SLAG
PHASE REACTION HEARTH
GASES AND SOME SUSPENDED MOLTEN PRODUCTS FROM SECONDARY SHAFT
ENRICHED WHITE METAL
COPPER TO FURTHER TREATMENT AS REQUIRED

Figure 2. Britcosmaco process.[1]

pyrometallurgical treatment, energy requirements are lower, total gas volume is smaller, and SO_2 concentration in the off-gas is greater.

Reference

1. Price, F.C. Copper Technology on the Move. Engineering and Mining Journal, pp. RR-WW, April 1973.

2.3 TORCO PROCESS[1,2]

The Torco process has been used in Mauritania and Zambia to recover copper from silicate ores such as dioptase and chrysocolla, which cannot be extracted from the gangue rock by basic flotation methods. The process is based on the discovery in 1923 that copper silicates form growths of elemental copper when they are crushed, mixed with carbon and sodium chloride (common salt), and smelted in an inert atmosphere. Figure 3 is a basic flowsheet for a Torco plant. Coarse ore from the mine is crushed, dried, and ground. Ground ore is mixed with coal for the reaction and heated in a fluidized bed reactor. The preheated material from the first stage reactor overflows into a second fluidized bed, where salt and additional coal are added. Proper temperature and retention time result in the formation of copper granules. The mixture is quenched in water and ground, and the copper is separated by flotation. The low-grade copper product is mixed with feed to a conventional smelter.

Exhaust gases from the fluidized bed reactor pass through cyclones. After further particulate removal, the gases are discharged to the atmosphere, and solids trapped by the gas cleaning equipment are fed back to the reaction vessel.

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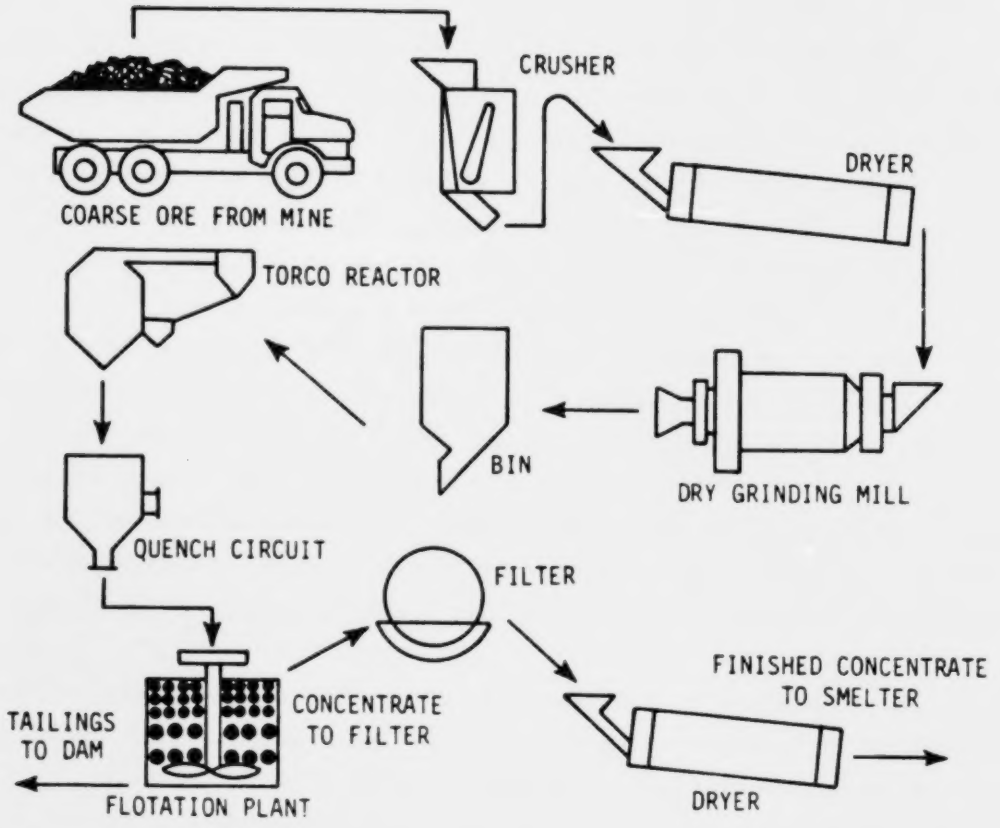

Figure 3. Torco process.[1]

2. Opie, W., et al. Selective Recovery of Copper From Copper-Nickel Sulfide Concentrates by Applying Segregation Technology. Metallurgical Transactions B. Vol. 10B. American Society for Metals and the Metallurgical Society of AIME, New York, March 1979.

2.4 WORCRA PROCESS

The WORCRA process, developed by Conzinc Riotinto of Australia, Ltd., is a continuous direct smelting process for copper concentrates. Experimental evaluation of WORCRA began in early 1963 in a pilot plant located in Cockle Creek, New South Wales, Australia. Encouraging results lead to the construction of a larger test furnace in Port Kembla, New South Wales. Trial tests indicate that the process can work on a larger scale.[1-3]

Copper concentrates are smelted to matte, matte is converted to metal, and slag is cleaned in separate zones of an elongated hearth-type furnace. Concentrates and flux are added in the mildly oxidizing smelting zone at an angle which ensures particle penetration into the melt and aids in the continuous circulation of matte and slag. As illustrated in Figure 4, concentrates are occasionally added in the converter zone to help control magnetite formation.

Slag generally moves countercurrently to the matte, and iron and other unwanted materials are continuously transferred to the slag after oxidation. Copper in the slag reverts to the matte phase by interaction with iron sulfides in the matte.

Moving slowly through the smelting and converting zones, matte is lanced with air (or oxygen-enriched air), causing conversion to white metal and then to copper. If oxygen is not used, lance air and combustion air preheaters are required, as are a larger furnace, boiler, and electrostatic precipitator (ESP). In the converting zone, the hearth slopes downward, and copper passes continuously to the "copper well," which overflows

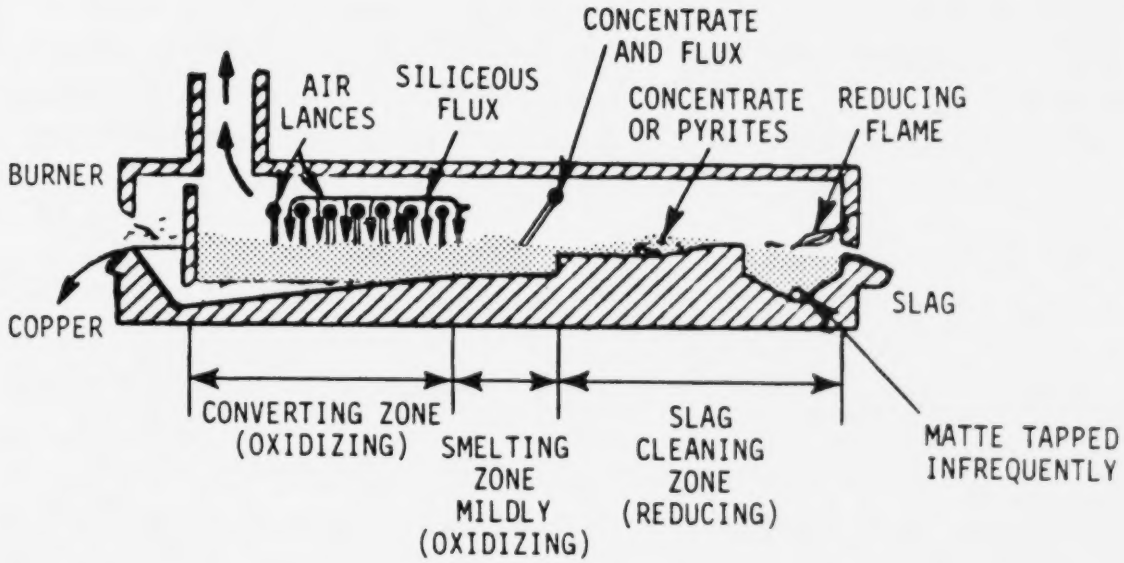

Figure 4. WORCRA furnace.[1]

with low-grade blister copper product. Extensive fire refining or converter processing may be required before casting.

The WORCRA furnace yields a constant stream of gas with an average sulfur dioxide (SO_2) content of 10 percent; use of oxygen-enriched air increases the SO_2 content.[4] Furnace gases can be used for waste heat recovery, and dust can be recovered before the gases are sent to a sulfuric acid plant or otherwise treated.

Capital costs for a WORCRA plant are expected to be 20 to 30 percent less than for a reverberatory furnace/converter plant with a similar capacity. Lower operating costs are also predicted, depending upon local variations in costs for fuel, power, and labor.[1-3] Fuel consumption by a WORCRA plant should be 50 to 60 percent of the operating costs of a conventional reverberatory furnace/converter plant of equivalent production rating.[1-3]

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Verney, L.R. Pyrometallurgy. Journal of Metals, 29(3):16-18, March 1977.

2.5 CONTINUOUS FIRE REFINING FURNACE[1]

A new process of continuous metal refining that involves supersonic injection of oxygen has reportedly been developed by KHD Industrieanlagen A.G. of West Germany. After preliminary experiments, KHD began construction of a pilot plant. At last report, the plant had been completed, but had not achieved totally satisfactory results.

Blister copper is introduced to the furnace and passes into a settling hearth. The melt overflows from the settling hearth to the oxidation hearth, where pure oxygen is injected through lances at 1800 km/h countercurrently to the metal flow. Slag from this stage is drawn off continuously. After oxidation, the melt underflows to the reduction hearth, where propane is injected for final refining. The metal, as illustrated in Figure 5, exits the triple hearth furnace as fire-refined anode copper.

Reference

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2.6 VACUUM REFINING[1]

Vacuum refining has been used in the steelmaking process since 1952, and Japanese researchers have recently attempted to apply the technique to production of nonferrous metals, especially copper. Literature on the process is sparse, but a brief discussion follows.

Figure 6 shows four possible applications of vacuum refining to the copper smelting process. The method can be applied to the refining of blister copper and matte. Ladle refining can be used to replace a conventional fire refining furnace, although the sulfur and oxygen content of the blister copper must be carefully controlled. The continuous treatment of copper is also a possible application of vacuum refining. Subsequent electrolytic refining is required in any application.

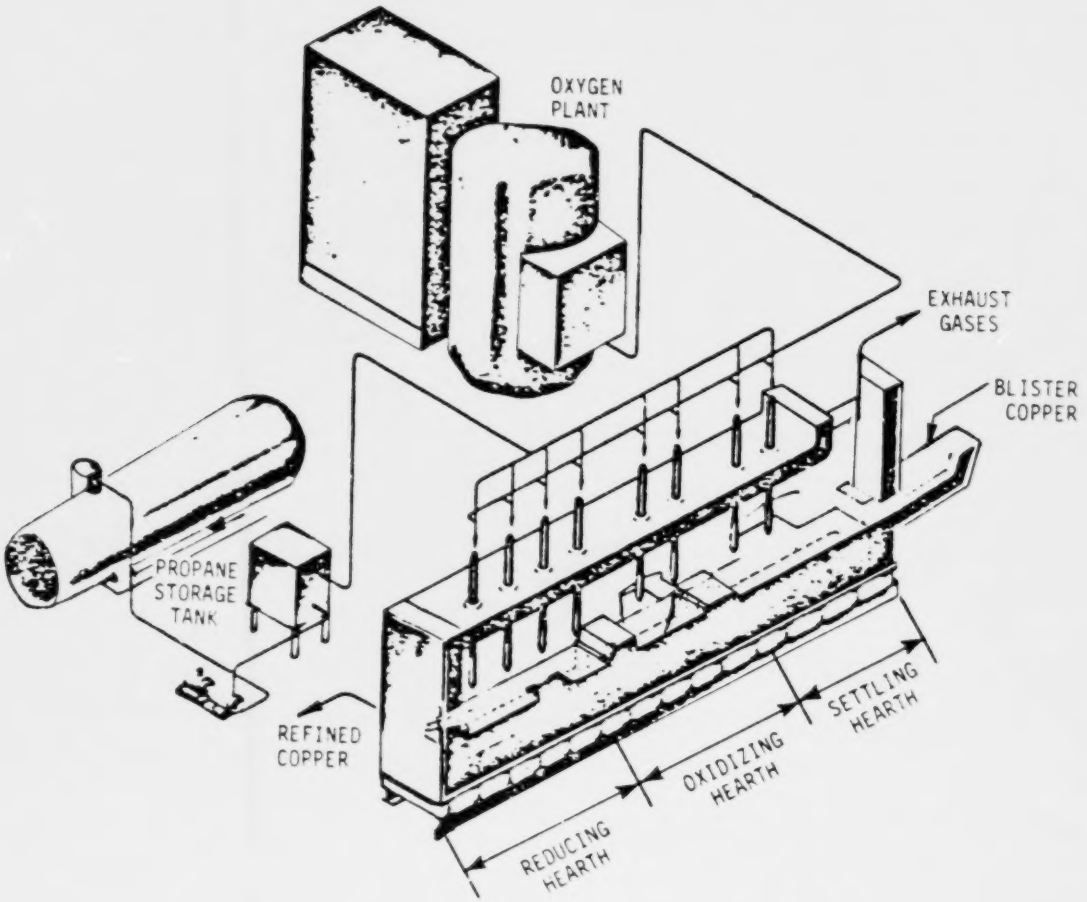

Figure 5. Continuous fire refining furnace.[1]

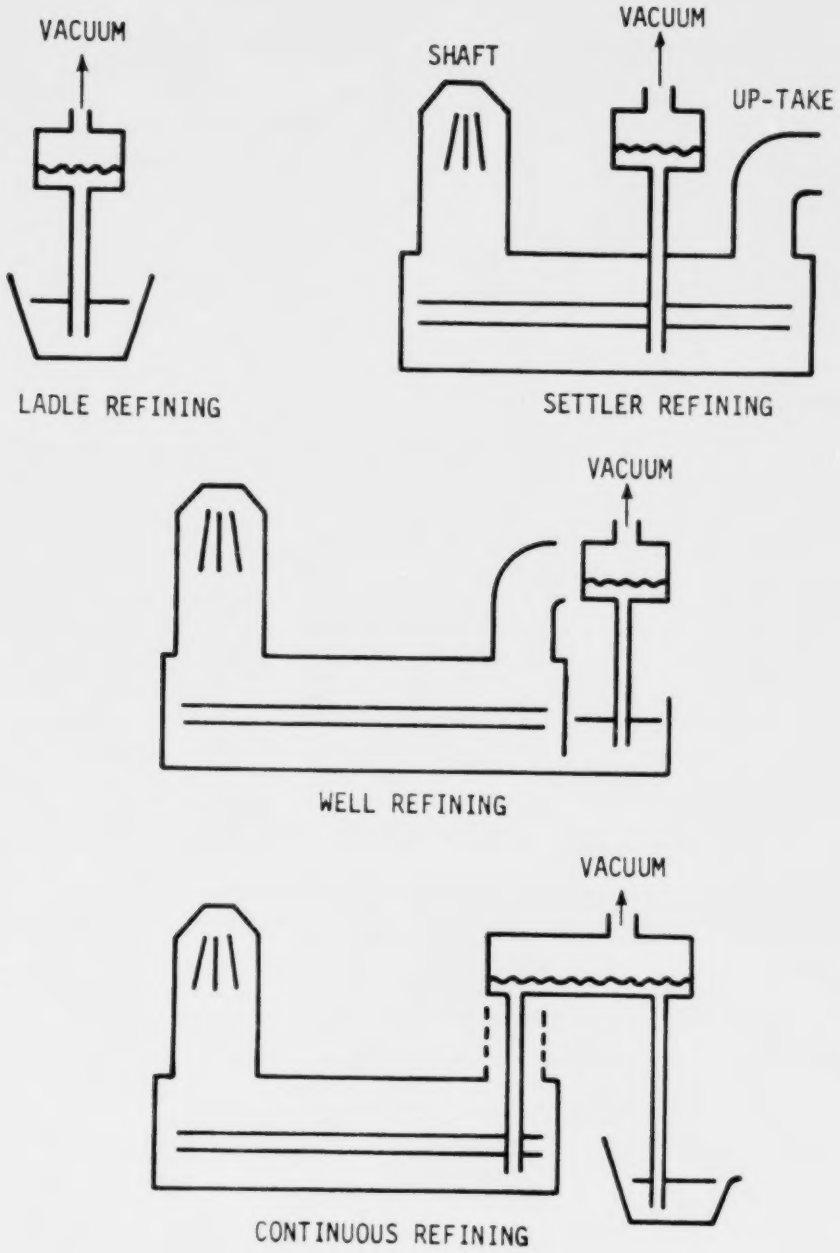

Figure 6. Possible applications of vacuum refining to the copper smelting process.[1]

Tests have shown that treatment of blister copper by vacuum refining rapidly removes sulfur and oxygen as sulfur dioxide. Adequate recirculation of the molten copper can remove 60 to 80 percent of the lead, 30 to 50 percent of the zinc, and 5 to 20 percent of the arsenic and antimony.

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2.7 EXTENDED ARC FLASH REACTOR

Canadian scientists have developed a new electric furnace for the direct carbothermic reduction of powdered ore and dusts. Although particularly applicable to the production of iron, the furnace can be applied to the smelting of nonferrous metals. As an outgrowth of work to improve the performance of electric arc furnaces, the Extended Arc Flash Reactor is offered by Tibur Metals, Ltd., of Hamilton, Ontario, Canada.[1]

As shown in Figure 7, the furnace consists of four sections: (1) a rotary preheater, (2) a column or flash reactor, (3) an extended arc zone, and (4) the hearth. The rotary preheater brings incoming charge (concentrate and coal) into contact with hot exiting flue gas containing carbon monoxide. The charge is dried and heated to approximately 800°C. The feed then enters a vertical shaft leading to the hearth, where 50 to 60 percent of the reduction occurs and the temperature increases from 800° to 1500°C.[1]

Hollow electrodes are used to inject argon gas into the electric arc. The gas is ionized and forms an extremely hot plasma, which can reach temperatures of 5000°C. This plasma extends the arc by which heat can be transferred to the charge as it passes through this zone. High temperatures within the plasma ensure reducing conditions in the flash zone, the plasma itself, and the hearth where final reduction occurs.[1]

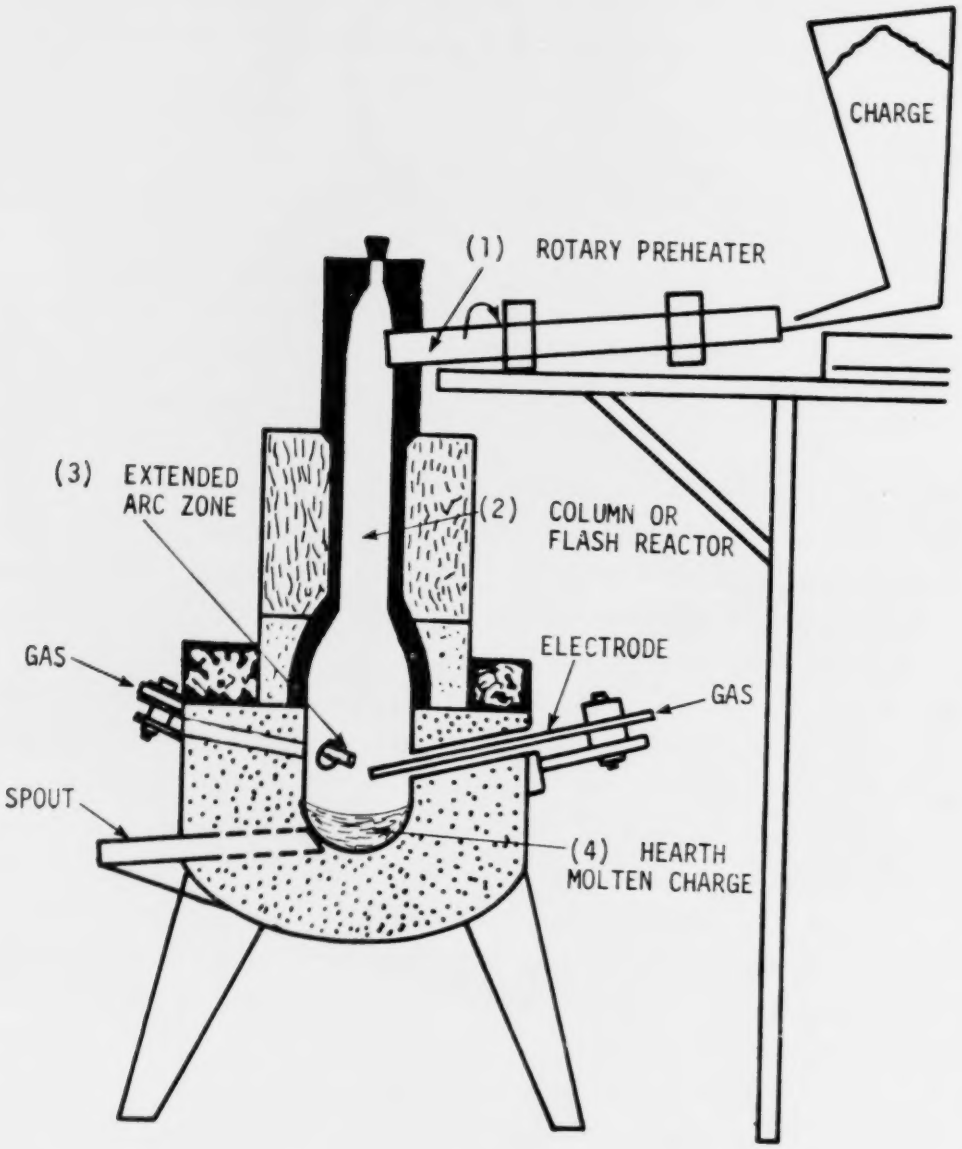

Figure 7. Schematic view of a laboratory unit showing components of the Extended Arc Flash Reactor.[1]

The advantages of a stabilized extended arc include reduced electrode consumption, reduced refractory wear, improved power factor and control, improved heat transfer, and reduced acoustical and electric noise.[2]

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2.8 INCO OXYGEN FLASH SMELTING

The International Nickel Company (Inco) of Canada developed the oxygen flash smelting process in the 1940's to treat copper and nickel concentrates. By the early 1950's, Inco had successfully demonstrated the method on a commercial scale at the Copper Cliff plant. During this same period, Outokumpu designed and demonstrated a similar flash smelting furnace, which has been successfully marketed in many countries, including the United States.[1,2]

The Inco oxygen flash smelting furnace is much simpler in design than the Outokumpu furnace and uses pure oxygen for the oxidizing medium, whereas the Outokumpu furnace uses preheated or oxygen-enriched air. The Inco furnace is essentially a reverberatory furnace with an uptake shaft extending the length of the furnace roof.

Figure 8 illustrates the Inco process. A wet concentrate-flux mixture is introduced through a rotary sealing feeder to the fluidized bed dryer. Solid particles are dried while suspended in the upward stream of hot combustion gas. Moist gases and dry solids are separated in the two product fabric filters after they are drawn out through the dryer roof. The product fabric filters are reported to have a collection efficiency greater than 99.9 percent.[2]

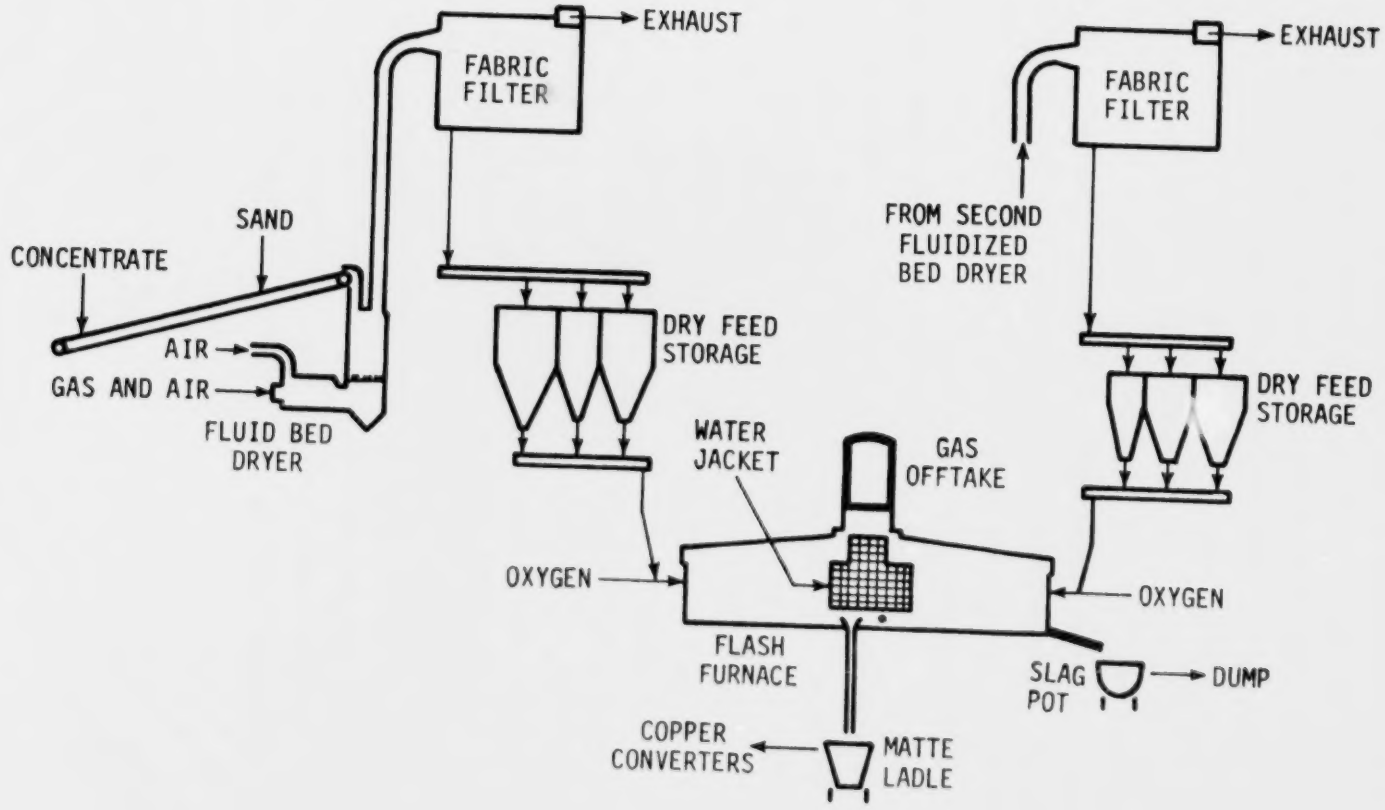

Figure 8. Inco process.[1]

The solids are withdrawn from feed bins and transferred by screw conveyors and gravity to the two burners located at each end of the furnace. Suspended in a horizontal flow of oxygen, the feed is injected into the furnace. Oxygen combines with some of the sulfur and iron to form SO_2 and iron oxides. A fayalite slag is formed by silica, which is contained in the flux and concentrate, reacting with the iron oxides. The remaining sulfur and metal fractions collect in the matte, which is transferred to one of three Pierce-Smith converters for production of blister copper. Almost all the oxygen is consumed during the process.[2]

Exiting furnace off-gases contain 83 percent SO_2, 13 percent nitrogen, 1.5 percent carbon dioxide, 2.5 percent argon, and <0.02 percent oxygen. About 2 to 3 percent of the feed exits as dust during smelting operations. The furnace gas cleaning system includes a settling and radiation chamber, a spray tower, three venturi scrubbers, and a wet electrostatic precipitator. After the gas stream is cooled and cleaned of particulates, the SO_2-laden gas is piped to an adjacent liquefaction plant. The Inco oxygen flash furnace emits less SO_2 and fewer impurities than a reverberatory furnace handling a typical concentrate for North America. In addition, the extremely small volume and high strength of the flash furnace off-gases blended with converter gases allow for a greater degree of control.[2] Other advantages of this process include simple engineering design, easy process control, and relatively low energy and capital requirements. The process, however, is not as amenable to concentrates with high impurity levels, because such levels can cause unacceptably high concentrations of impurities in the blister copper.[1,2]

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2.9 QUENEAU-SCHUHMANN PROCESS[1]

Professors P.E. Queneau and R. Schuhmann, Jr., have invented an environmentally clean process for the continuous production of nonferrous metals from sulfide concentrates. The Queneau-Schuhmann (Q-S) process is used in a pilot plant at Duisburg, West Germany. Galena concentrates are first oxidized and then reduced in a molten state in a single, sealed reactor. Rapid oxidation is accomplished by submerged injection of oxygen; reduction and total desulfurization can be obtained by submerged injection of a small amount of pulverized coal. As shown in Figure 9, bullion leaves the reactor at one end, and slag leaves at the other.

The capital and operating costs of a commercial Q-S installation are estimated to be considerably less than those of a conventional smelter with sinter plant and shaft furnace. Energy can be saved because the large amount of coke required for a conventional facility is replaced by a small amount of low-grade coal.

A Q-S unit also offers environmental advantages over a conventional smelter. The only process gases are those from the reactor, which contain about 20 percent SO_2 by volume. This concentration readily lends itself to sulfuric acid or liquid SO_2 production. Because a Q-S unit is compact and operates continuously, the volume of fugitive gases is relatively small, and they can be treated in two-stage precipitators, with resulting minor emissions of particulates.

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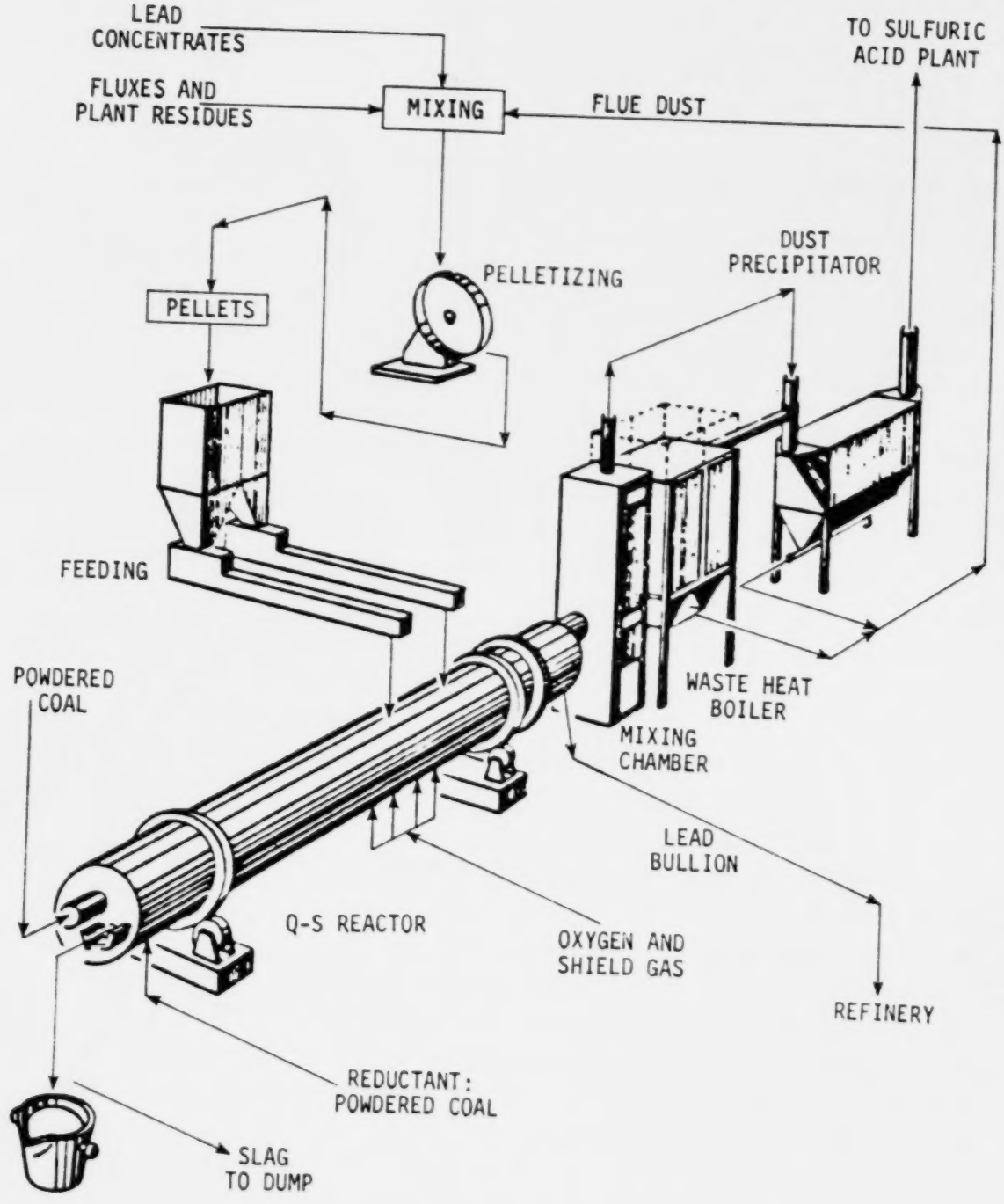

Figure 9. Schematic view of the Q-S process.[1]

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2.10 KIVCET PROCESS

The Kivcet process involves continuous smelting of complex sulfide concentrates with simultaneous production of lead, zinc, copper, nickel, and minor metals such as cadmium and tin. The process has been under research and development since 1963. After extensive tests, a 45-Mg/day pilot plant was constructed in the metal mining region of the Uzbekistan Republic in the Soviet Union. The first 272-Mg/day commercial-scale plant for smelting complex sulfide concentrates was built at Tashkent, and a 600-Mg/day plant is under construction.[1-3]

Sulfide concentrate, containing at least 25 percent sulfur, and oxygen are fed into a cyclone furnace (see Subsection 2.11), where the concentrate is autogenously roasted and flash-smelted in a suspended state. The products leaving the bottom of the cyclone reactor pass into a distribution chamber, where off-gases and melt are separated. The off-gases are cleaned of particulates and sent to the acid plant; the melt is routed to the electric furnace.[1-4]

The electric furnace is similar in design to a conventional furnace and is provided with water-cooled bottom and side walls. Settling takes place in the electric furnace in a reducing atmosphere, and addition of a reducing material such as hydrogen is

necessary. Matte containing copper, nickel, cobalt, and precious metals is periodically tapped and further processed by conventional methods. Zinc is volatilized in the electric furnace and may be condensed to metal or oxidized to produce high-grade zinc oxide. Figure 10 is a simplified flowsheet of the Kivcet process.[1-4]

Off-gases from the distribution chamber are very small in volume and high in SO_2 content. Approximately 80 percent of the sulfur in the concentrate passes into the off-gases, which contain up to 90 percent SO_2. The high-strength off-gases may easily be converted to elemental sulfur, sulfuric acid, or liquefied sulfur dioxide.[1-3]

Slag from the electric furnace contains very little entrained matte and can be discarded immediately without cleaning. Therefore, expensive and space consuming cleaning equipment is not necessary.[1-3]

Overall capital costs of a smelter using the Kivcet process are claimed to compare favorably with other high-technology processes. Elimination of agglomerating, sintering, and slag cleaning installations and simplification of gas cleaning and SO_2 capture systems help reduce costs.[1-3]

Before improvements in the electric furnace, energy consumption seemed relatively high because of excess heat loss from the water-cooled bottom and side walls. After modifications, the energy consumption of a Kivcet smelter with an annual capacity of 73,000 Mg of crude bullion is estimated to be 600 kWh/Mg of crude bullion.[1-3]

The recently developed CS variant of the Kivcet process uses a flash smelting shaft furnace instead of a cyclone furnace. This variant has been developed in the Soviet Union for industrial application in single-step autogenous smelting of lead sulfide concentrate with oxygen.[5,6]

Significantly less heat is liberated when smelting lead sulfide than when smelting a copper sulfide. Therefore, the

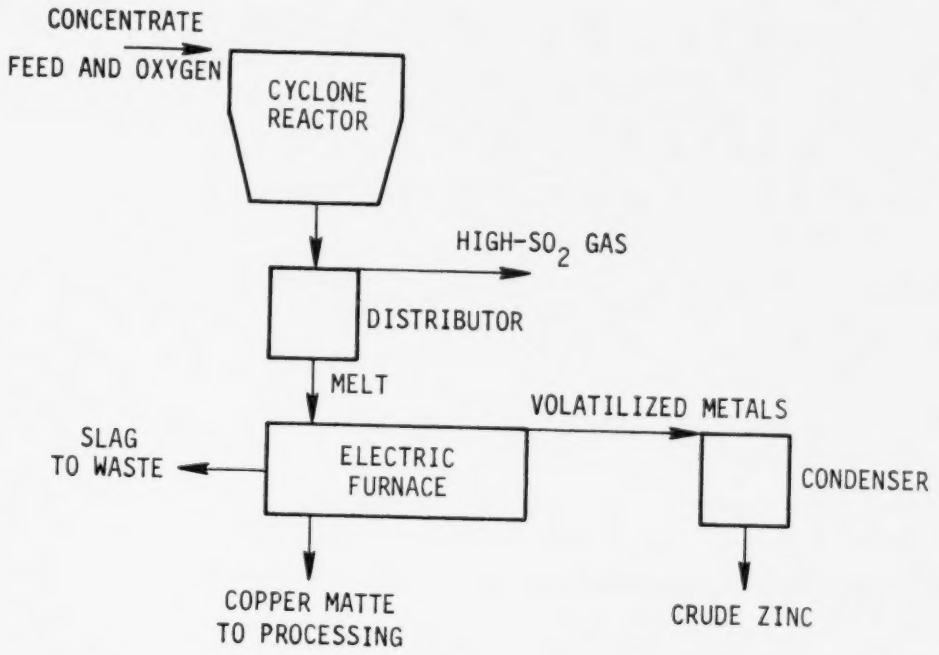

Figure 10. Simplified flowsheet of the Kivcet smelting process.[1]

great heat dissipation characteristic of the cyclone makes autogenous smelting of lead sulfide very difficult in a cyclone furnace. The electrothermal section of the variant CS process and the facilities for zinc recovery and gas treatment are identical to the standard Kivcet process; only the roasting/smelting section differs.[6]

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2.11 CYCLONE FURNACE SMELTING[1]

Humboldt Wedag of Germany, in cooperation with the Metal Research Institute of the Soviet Union, has developed the cyclone furnace smelting reactor utilized in the Kivcet Process. This reactor is suitable for recovering metal from nonferrous ores, oxide or sulfide concentrates, and metallurgical slags and residues. Reports indicate that metals can be volatilized in the elemental form or as compounds in compact, continuously operating, cyclone furnace smelters, which can fire a variety of fuels. Metals that cannot be volatilized can be upgraded to matte.

The key to this smelting technique is a cylindrical cyclone reactor. Feed smaller than 1 mm in diameter is charged to the reactor from the top, and a tangentially admitted fuel-air mixture moves the charge downward at high speed. The rapidly heated particles melt and deposit as droplets on the reactor walls by centrifugal force, but volatile matter escapes prior to this deposition. Gases and molten products are discharged from a central outlet at the bottom of the reactor; the gases then pass to a secondary combustion chamber, designed as a cooler, where carbon monoxide, volatilized metals, and metal compounds are subjected to secondary oxidation by admitting air. This chamber may also be used as a waste heat boiler. Waste gases are treated in an electrostatic precipitator and/or fabric filter to recover metal oxides.

Molten products collect in a settling furnace, where matte and slag are separated. The matte and slag can be tapped into ladles or separated continuously in a centrifuge designed for high-temperature operation.

The current maximum capacity of a cyclone furnace is approximately 275 Mg/day, but the capacity of an entire facility can be easily increased by use of several furnaces. These furnaces can be operated in a parallel fashion and require only one waste gas treatment system and one electric furnace.

A cyclone furnace smelter in Bolivia treats antimony sulfide to produce antimony trioxide. The sulfide is volatilized, and the antimony trioxide is captured in a fabric filter following an afterburning operation. The cyclone furnace is 0.85 m in diameter and 1.25 m long and can handle 36 Mg/day of ore, concentrate, and fluxes. Recovery efficiencies as high as 96 percent have been reported. A second plant is under construction in Bolivia and will be used to upgrade low-tin concentrates. The capacity of this furnace will be 100 Mg/day.

The processing of tin, lead-bearing shaft furnace slags, residues from neutral zinc leaching, or lead-zinc intermediate products from lead and zinc residues does not require an electric furnace to be used in conjunction with a cyclone furnace. When residues to be treated contain copper, silver, or gold, an electric furnace is required to separate slag from matte and concentrate these elements in the matte.

Bulk flotation concentrates containing copper, lead, and zinc can be upgraded by volatilizing the lead and zinc, which are recovered in the oxide form, and separating the enriched copper matte from slag in an electric furnace. Tests indicate that lead and zinc can be volatilized up to 90 percent, yielding a 70 percent metal oxide.

The major advantages of cyclone furnace smelting are the low capital and operating costs.

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2.12 TOP BLOWN ROTARY CONVERTER

The International Nickel Co. of Canada has adapted steel process technology (the Kaldo process) to nonferrous metallurgy in developing the top blown rotary converter (TBRC), which can smelt a variety of concentrates or byproducts. Boliden a.-b. of Sweden has carried out additional development of the TBRC, and several commercial-scale plants are in use, including two in Sweden and one each in Ontario and British Columbia, Canada.[1-3]

Five TBRC production processes have been investigated and tested by metallurgists in laboratory, pilot-scale, and commercial-scale plants. These processes have been tested with dust containing lead-zinc, copper matte or concentrate, copper converter slag, lead concentrate, and nickel concentrate.

Figure 11 shows a TBRC, which is claimed to increase operational flexibility through control of both temperature and turbulence and maintain high thermal efficiency. After complex

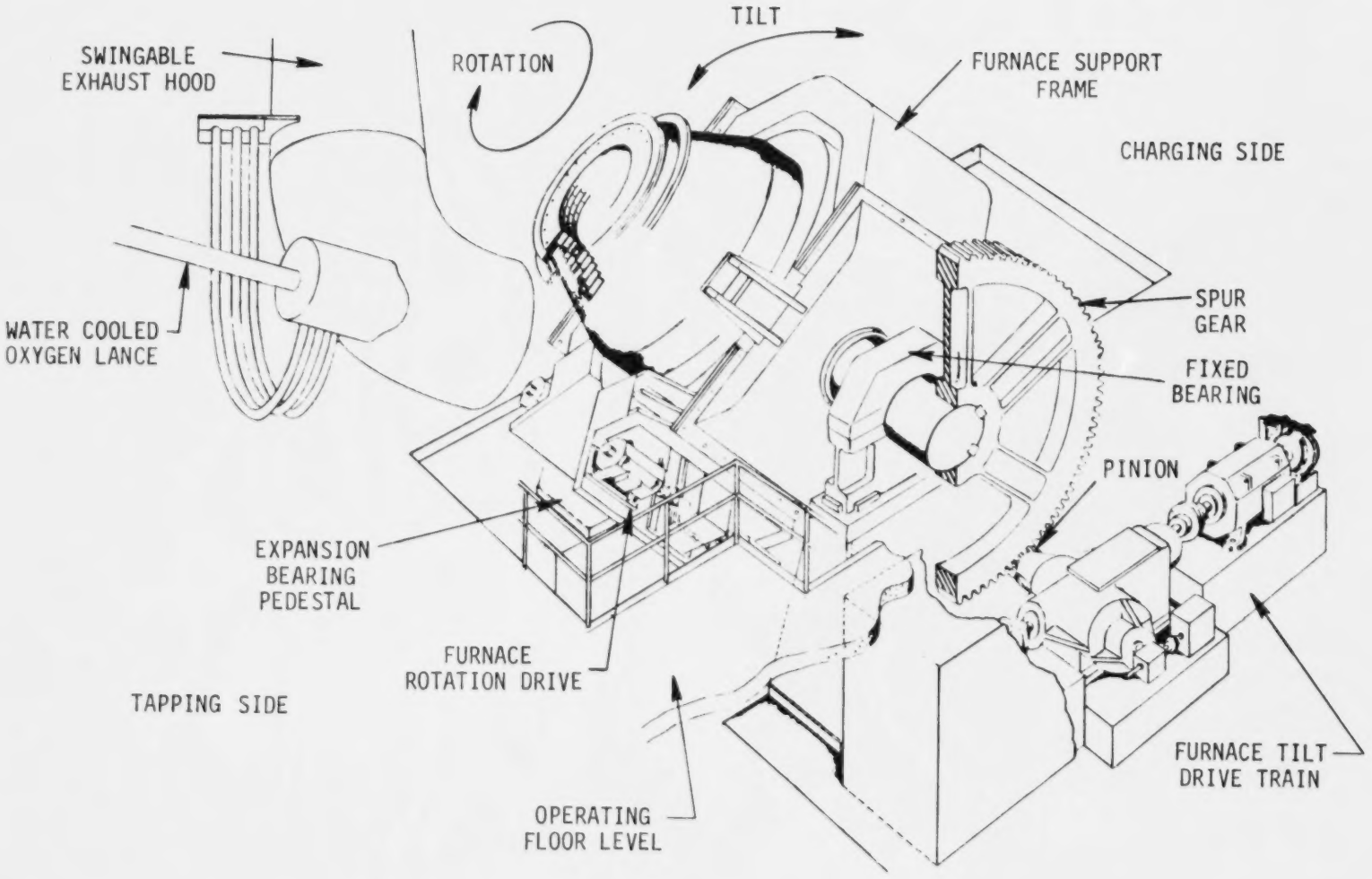

Figure 11. Top blown rotary converter.[2]

copper concentrates are dried and agglomerated in a briquetter, they are fed to the TBRC, which contains a molten sulfide bath. The vessel atmosphere is controlled by injecting natural gas and oxygen-enriched air into the molten mixture through a water-cooled lance. White metal is then sent to a second TBRC for further oxidation and elimination of impurities.[1-3]

The furnace rotates constantly, providing thorough contact between the gas and furnace contents and ensuring even distribution of heat. Oxygen efficiency greater than 95 percent can be obtained by adjusting rotational speed and angle of the injection lance.[3] The molten metal can be removed from the furnace and separated by electrolytic refining. Slag is left in the vessel for recovery of valuable metals upon addition of new concentrate.

In the Boliden lead smelter, the TBRC is used to treat pelletized lead bearing dusts and residues and reduce high-grade lead concentrates.[4,5] At Rönnskär, Sweden, the TBRC is housed in a separate building, which is completely enclosed by a ventilation casing; the casing incorporates a bag filter.[1] With oxygen enrichment, the exhaust gases contain up to 50 percent SO_2 and little particulate matter. The Afton mine/smelter complex in British Columbia sends waste gas from the TBRC through a combination of electrostatic precipitators for particulate removal and a dual-alkali scrubber for SO_2 removal.[3] A close-fitting exhaust hood fits over the mouth of the converter during loading, smelting, and converting operations.[6]

The advantages of the TBRC include lower particulate loadings, decreased fugitive emissions, and greater SO_2 concentrations. The batch-type operation, however, does not produce a continuous stream of gas. Work at the Inco Copper Cliff Nickel refinery in Ontario indicates that particulate emissions are directly related to the number of converter revolutions per minute. Decreases from 25 to 5 rpm during charging and blowing and from 30 to 15 rpm during reduction reduce stack loss of metal values by half and improve refractory performance.[7]

Data indicate that the capital cost of the TBRC process is considerably less than that of conventional smelting techniques. The operating cost is also less because of lower maintenance, labor, and energy requirements.[2,3]

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2.13 IMPERIAL SMELTING PROCESS

The Imperial Smelting process has long been a competitive means of producing lead and zinc and should continue to be economically viable because it allows smelting of complex lead-zinc ores.[1] Although the process is used in 10 countries, it does not appear applicable to many U.S. concentrates.

The process can vary, but the vertical shaft blast furnace is the main item of any Imperial Smelting facility. The Societe Miniere and Metallurgique Pennarroya facility in Noyelles-Godault, France, first operated an Imperial furnace in 1962 as a replacement for a horizontal retort. The furnace can produce 90,000 Mg of zinc each year. Figure 12 shows the furnace design and process flow.[2]

At the Noyelles-Godault plant, zinc, lead, and zinc-lead concentrates are sintered in a Dwight-Lloyd machine to remove sulfur. A sulfuric acid plant treats the off-gas, and volatilized cadmium is treated separately. The sinter is fed with fluxes to the top of the furnace, and metallurgical-grade coke is charged on top. The blast enters the furnace through 15 steel tuyeres, each 90 mm in diameter. The blast temperature of 900°C is obtained with two cowper stoves that fire furnace gas.[2] The lead and zinc oxides are reduced by coke combustion gases; lead metal is produced in the upper portion of the furnace shaft and sinks toward the bottom. The zinc oxide is reduced in higher-temperature zones lower in the furnace, and the volatilized metal, which leaves the furnace with the off-gas, is captured in

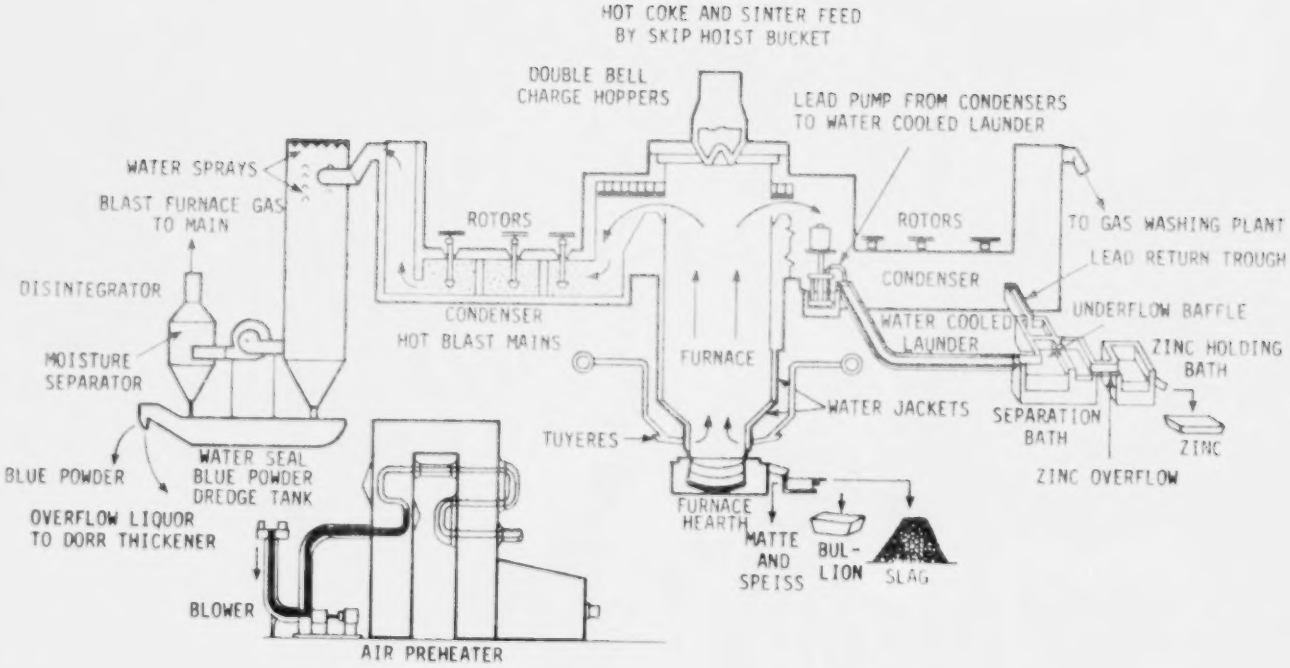

Figure 12. Imperial Smelting furnace.[2]

condensers. The slag melts in a zone above the tuyeres and sinks with the lead. Minor elements (e.g., cadmium) either vaporize and exit with the zinc in the off-gas or sink with the lead and slag.[2]

Under the tuyeres is a hearth which receives the bullion, slag, matte, and speiss. These materials are tapped into a forehearth approximately every 90 minutes. Because of different specific gravities, the bullion and slag separate in the forehearth. The bullion is tapped into a ladle and cast into 3 Mg ingots, and the slag overflows into a granulation system. The matte and speiss layer builds up until it is tapped; this occurs once every 5 or 6 times the bullion is tapped.[2]

Lead is the washing fluid used in the condensers to capture the zinc. Gases meet a countercurrent lead spray, which is projected by rotor blades in the condensers. The zinc is carried out of the condensers by the lead, and the mixture is separated in cooling launders.[2]

The Imperial Smelting process is very flexible. The ratio of lead to zinc in the sinter can vary considerably, and oxide or sulfide concentrates or ores can be used. Reducing conditions in the furnace can be varied, as can the operating conditions in the condensers.[2]

The Imperial Smelting process offers no environmental advantages over other techniques, and lead pollution remains a concern.[1] The process does, however, allow treatment of complex ores and use of coke rather than electricity.

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2.14 BOLIDEN DIRECT REDUCTION PROCESS

Boliden a.-b. has developed a process for the direct smelting of lead concentrates and used it for some time at Rönnskär, Sweden. Several process variations, including the use of an electric furnace and TBRC's, have been tried. The capacity of the Rönnskär facility is about 150 Mg of lead per day.[1,2]

Dried, unsintered lead concentrates (72 percent lead) and recycled flue dust are blended and charged to an electric smelting furnace by variable-speed screw conveyors through pipes into openings in the roof of the furnace.[1,2]

Nozzles for combustion air are inserted through the charging openings in the top of the furnace. Horizontal jets of air are aimed at the incoming material, and a cyclone-like suspension is formed. This action provides sufficient time for burning the bulk of the sulfur and oxidizing the iron and zinc. Recently,

oxygen enrichment (10 percent) has been instituted.[2] The moisture content of the concentrate, however, must be below 2 percent for proper reaction. Most of the lead sulfide is reduced to metallic lead and sulfur dioxide. Because sufficient heat is not generated to sustain this reaction, additional electrical energy must be supplied.[1-3]

The solid and molten products are collected in the slag, where the reactions are completed, and the slag and lead are then separated. Coke breeze is applied to the surface of the slag bath to reduce the lead oxide content. Dross and matte from downstream converters are crushed and charged with limestone and dust from the waste heat boiler to the slag bath. The slag is then electrically heated to about 1350°C, and lead is tapped directly to one of two converters in 70-Mg batches. The converters also receive recycled dross from the refinery.[1]

After a blow lasting about 40 minutes at a rate of 85 m^3/min, the lead is allowed to cool in the converter for 7 to 9 hours. During this period, molten lead-copper matte and dross are separated from the crude lead. The lead is then transferred to the refinery in ladles, and the dross is crushed with most of the matte and recycled to the furnace.[1]

Furnace slag is tapped in 18-Mg batches and transferred by ladle to a fuming furnace.[1] Gases leave the furnace at around 1050°C and are cooled in a waste heat boiler and by air cooling. After passing through a dry electrostatic precipitator, the SO_2-laden gases enter a sulfuric acid plant. Dust is continuously recycled.[1]

The direct reduction process eliminates some problems associated with traditional lead smelting techniques, such as high energy consumption and large volumes of gas with low SO_2 concentrations. Whereas traditional processes can require 2000 kWh/Mg lead bullion smelted, the Boliden direct reduction process needs only 1050 kWh/Mg.[2] The lead bullion produced, however, contains about 3 percent sulfur, which is removed in the converters.

A new direct reduction process recently developed by Boliden uses a TBRC (see Subsection 2.12). The main feature of the new process is autogenous smelting of dried concentrates (72 percent lead) with highly enriched air (60 percent oxygen) in a TBRC. The energy consumption for the oxygen supply (150 m^3/Mg lead) is about 70 kWh; therefore, energy demand for the smelting step is decreased to about 70 percent of the energy demand of the old Boliden reduction process.[2,4]

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2.15 BERGSØE WHOLE BATTERY SMELTING PROCESS

In 1975, Paul Bergsøe and Son A/S began smelting whole storage batteries at Golstrup, Denmark. This process eliminates the dangerous job of breaking battery cases.[1] Bergsøe now plans to construct a $14-million facility using this technology in St. Helens, Oregon.[2]

The Bergsøe process, which is used in Denmark and Sweden, involves feeding whole batteries, battery scrap, lead dross,

sludge, coke, iron, flux, and agglomerated dust to the top of a water-jacketed shaft furnace similar to blast furnaces at a primary lead smelter. Batteries are cracked, spent acid is drained and neutralized, and soluble metals are precipitated.[1,3,4]

The furnace is equipped with two rows of tuyeres, one row on either side, through which preheated (500°C) oxygen-enriched air is injected. Preheated air has not previously been used in this manner in secondary lead production. Special covers are fitted over the tuyeres to minimize fugitive emissions during punching. Four hooded slag taps and one hooded lead well are located at the bottom of the furnace. The lead is cast into 1-Mg ingots in pneumatic equipment.[1] Under proper conditions, the furnace can smelt continuously for many months.

The furnace off-gases are treated in an afterburner, combined with cooling air, and routed to a fabric filter of Swedish design that uses a felted polyester cloth. The afterburner eliminates the need for a tall stack. Collected dusts are conveyed in an enclosed system to two flash agglomeration furnaces before recycle. (Construction and operation of the flash agglomeration furnaces are described in Subsection 5.8.) Gases collected by the tap hole and lead well hoods are routed to the fabric filter. The stack emissions have been reported to contain 200 ppm SO_2, 5 to 10 mg particulates/m^3 gas, 3 to 5 mg lead/m^3 gas, and trace quantities of chlorine.[1,3-5]

The whole smelting process is electronically controlled and emissions are monitored. The smelter area is periodically rinsed and the collected rinse water is treated by precipitation with soda ash. The effluent is treated at a municipal wastewater facility, and the sludge is recycled to the shaft furnace.[1]

The smelter produces a slag with a lead content of 0.6 to 1.0 percent lead; its disposition is not specified. The matte contains 25 percent sulfur, 8 percent lead, and some copper and can be sold to a lead smelter equipped with a roaster.[1]

Smelting whole batteries requires about 50 percent less coke than conventional techniques because of the energy derived from the cases. Use of preheated, oxygen-enriched air also reduces coke consumption, but the preheater requires oil.[1] Additionally, the flash agglomeration furnace consumes about 25 liters of oil per hour.[3] Electrical consumption is about 80 kWh per megagram of charge.[5]

The capital cost of the Golstrup facility is reported to have been $731,452 in 1975, and the operating cost equals $37.95 per megagram of output from the shaft furnace.[1]

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2.16 OLIFORNO WHOLE BATTERY SMELTING PROCESS[1]

Accumulatoren Fabrik of Oerlikon, Switzerland, operates a secondary lead facility that treats whole batteries in a kiln. The metal/slag product, which can be handled hygienically, is granulated and can be smelted at a high throughput rate in a short rotary furnace.

The Oliforno process produces more flue dust than does the Bergsøe process, and much of the fine sulfur in the feed passes into the off-gases. The gases are routed through an afterburner and indirect cooler before they are treated in an ESP.

Reference

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2.17 PYROMETALLURGICAL SLAG TREATMENT[1,2]

Russian scientists have developed a pyrometallurgical method of treating molten slag for the extraction of zinc, lead, tin, and other nonferrous metals. This process is similar to the slag fuming technology employed at many U.S. lead smelters. This process, however, uses combustion products from natural gas burned outside the furnace as a reducing agent, rather than pulverized coal injected directly into the furnace.

Molten slag is fed into the slag fuming furnace, and combustion products are blown over the melt by means of a special device developed for gas burning and feeding. The resulting gas stream is cooled in a waste-heat boiler, where coarse metal sublimates are collected. The off-gas is then sent to dust collecting and gas cleaning equipment. Figure 13 illustrates the slag fuming process. Metal values recovered can be further concentrated and processed by known methods.

Two plants in commercial operation in the Soviet Union treat slags containing nonferrous metals.

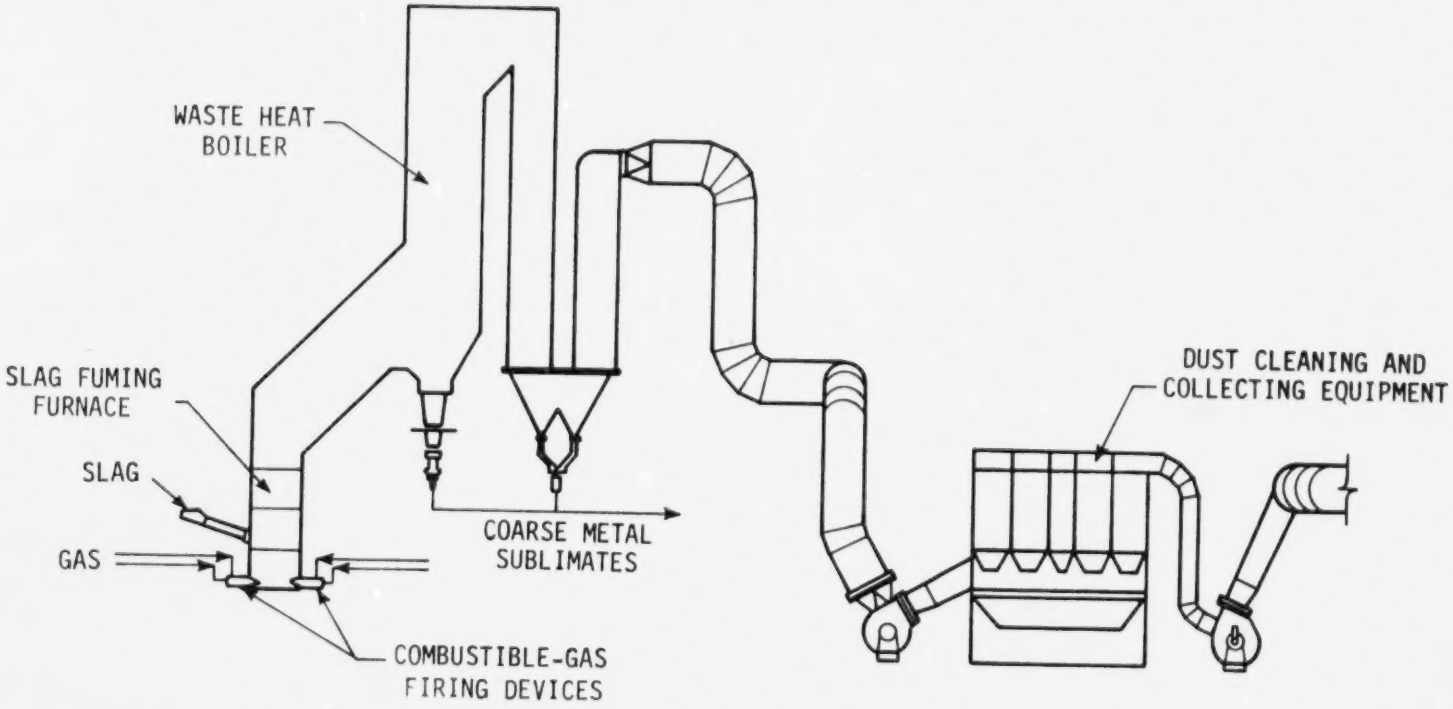

Figure 13. Slag fuming process.[2]

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2.18 SEA NODULE PROCESSING

Processing technology for the recovery and extraction of deep-sea ferromanganese nodules is beginning to unfold. Several processes have been developed on a laboratory scale; others are still on the drawing board. The process technologies ultimately used will depend on which metals can be economically recovered. Nickel, cobalt, copper, and manganese are all present in quantities that make recovery attractive. On the average, Pacific Ocean nodules are composed of 27 percent manganese, 6 percent iron, 1.5 percent nickel, 1.3 percent copper, and 0.25 percent cobalt.[1] Most of the manganese will be discarded to avoid glutting the market.[2] Several large-scale processing experiments are planned in the next several years, and these marine resources should be developed within the next 10 years. A discussion of process technology already under development follows.

The Institute of Metallurgy and Electrometallurgy at Aachen University, West Germany, has been investigating a process for the elemental separation of manganese nodules. Manganese nodules, ground to particle size from 60 to 120 μm, are treated in a plasma reduction furnace with hollow electrodes. The reaction particles are obtained as agglomerated particles or as metal and slag phases.[3] This process has the following advantages:

Weight reduction is carried out near the actual location of the nodule deposits.
Reaction rates are faster.
The size of the particles is greater.

The resulting products can be processed further in hydrocyclones and by selective flotation.

A hybrid process in operation in Canada to recover copper, nickel, and cobalt from sea nodules includes a pyrometallurgical reduction kiln followed by smelting in an electric furnace, and then hydrometallurgical leaching in an oxygen atmosphere to extract the metals. Although this highly specialized process is intended primarily for nickel recovery, it also recovers copper equivalent to 60 percent of the weight of the nickel. The estimated capital cost of a commercial-scale plant is $540 million.[4]

Another process, developed in Hawaii, recovers copper and nickel by hydrometallurgical techniques. The ferromanganese nodules react with an aqueous solution of oxalic acid, which results in the reduction of Mn (IV) to Mn (II) and the subsequent evolution of CO_2 and the solubilization of all the transition metals. Nickel and copper are selectively extracted from the solution with a commercially available reagent, LIX 64N.[1]

Kennecott Copper Corporation has developed a low-temperature ammonical leach process to extract metal values from manganese nodules. Nodules are wet-ground to a fine mesh, and carbon monoxide is added to the slurry as a reducing agent. A countercurrent decantation wash, carried out in a series of thickeners, further solubilizes the metal values. The decant solution contains all the copper, nickel, and cobalt, while the tailings contain the manganese.[4] The estimated capital cost of a commercial-scale plant is $340 million.[2]

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2.19 AUTOMATIC TUYERE PUNCHING[1]

As part of an effort to boost copper production and increase sulfur recovery at its Legnica smelter, the Kombinat Gorniczo-Hutniczy Miedzi (KGHM) of Poland has developed an automatic, pneumatic-converter tuyere puncher. The compact punchers are installed on 33- and 45-Mg Hoboken converters at Legnica and an 80-Mg Hoboken converter at Glogow. They also can be installed on Peirce-Smith units, as some domestic smelters practice automatic punching.

The manual removal of slag accretions in tuyeres is a slow, hazardous task requiring extra manpower. Mechanical punchers are available, but their use is restricted by the limited space on the tuyere side of the converter, they require an additional operator, and they are quite expensive. The KGHM automatic tuyere puncher eliminates these problems.

The automatic puncher is composed of three assemblies: a frame assembly that allows the puncher to be moved from one tuyere to another, a punching assembly consisting of a punching rod and a pneumatic drive, and a power supply and automatic electric/pneumatic control unit. Depending on such local conditions as the space on the converter tuyere side, a puncher weighs 1.5 to 2.5 Mg and is about 2 to 3.5 m long.

The unit can be operated in three different modes. In the fully automatic mode, the signal activating the puncher reduces the airflow through the tuyeres below a preselected value. In this mode, any tuyere can be eliminated from the punching cycle. If, after one cycle the quantity of air actually blown into the converter remains below the preselected value, the cycle is repeated. Figure 14 illustrates this mode of operation.

In the semiautomatic mode, the converter operator simply presses a button and a complete punching cycle is performed. If desired, individual tuyeres can also be eliminated from the cycle in this mode.

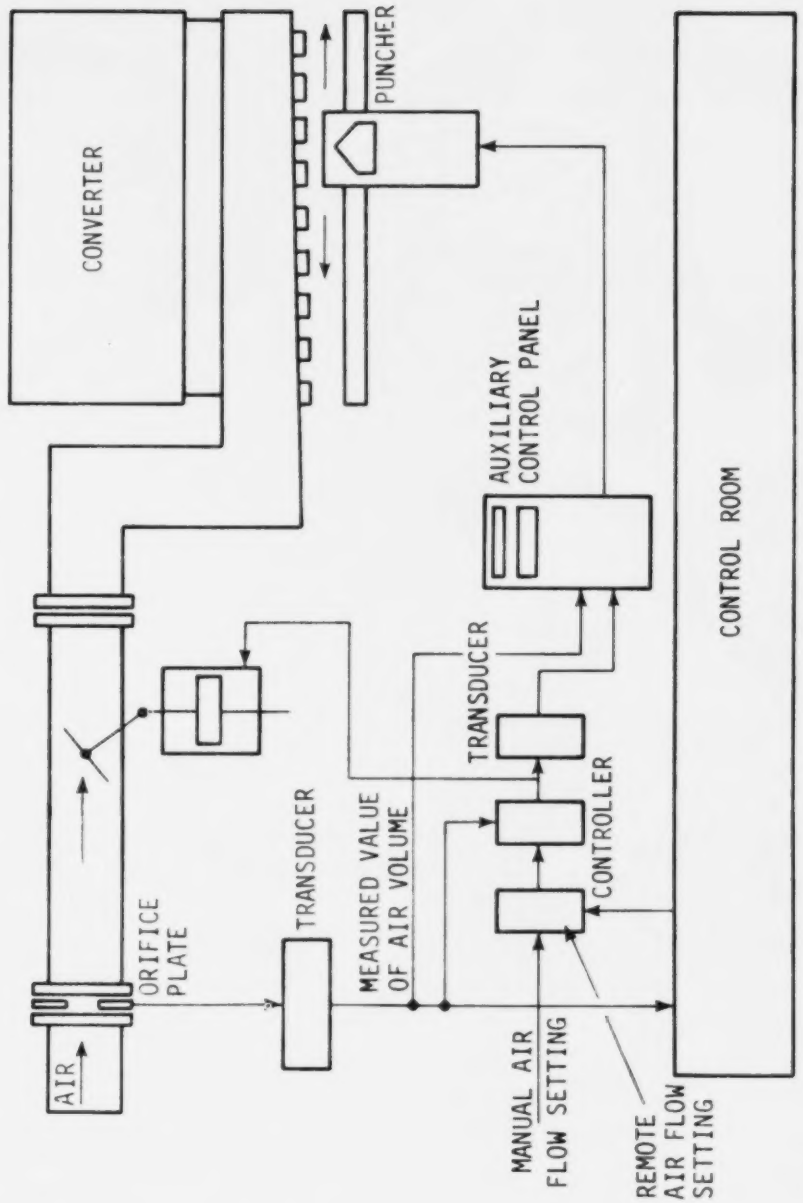

Figure 14. Automatic tuyere punching system.[1]

In the fully manual mode, the converter operator controls the unit with push buttons that move it to the left or right and activate the puncher.

It requires about 3 to 4 seconds to clean one tuyere, and move the puncher to the next tuyere. Therefore, the punching cycle at a 45-Mg Hoboken-type converter equipped with 28 tuyeres lasts less than 2 minutes, and no special operator is required.

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SECTION 3

HYDROMETALLURGICAL PROCESSES

3.1 MINEMET PROCESS[1]

Minemet Recherche has patented a hydrometallurgical process for the recovery of metals from sulfide ores and concentrates. The process, developed on a laboratory scale, is designed to recover copper from chalcocite, covellite, and chalcopyrite. In this process, which is illustrated in Figure 15, copper concentrate is first roasted to remove impurities, and then selectively leached by cupric chloride dissolved in a suitable solution, such as an alkali or alkaline earth chloride, ammonium chloride, or ferrous chloride. During this leach, sulfur associated with the ore is converted to the elemental state and remains in the leach residue for later recovery.

After the leach residue has been filtered out, the leach solution containing cuprous chloride and ferrous chloride is separated into two streams. The iron is precipitated as goethite by simple oxidation of the leach solution by air. The dissolved copper is recovered by solvent extraction and electrowinning. After the copper has been extracted the remainder of the solution is bled off for the recovery of other metals.

Elemental sulfur remaining in the leach residue may be recovered easily, by flotation or fusion, for internal use or for sale. After the sulfur is removed, the leach residue still contains pyrite, which could be an unstable solid waste.

The purported advantages of the Minemet process are high copper recovery, recovery of iron in the form of geothite and elemental sulfur (both marketable), low capital and operating

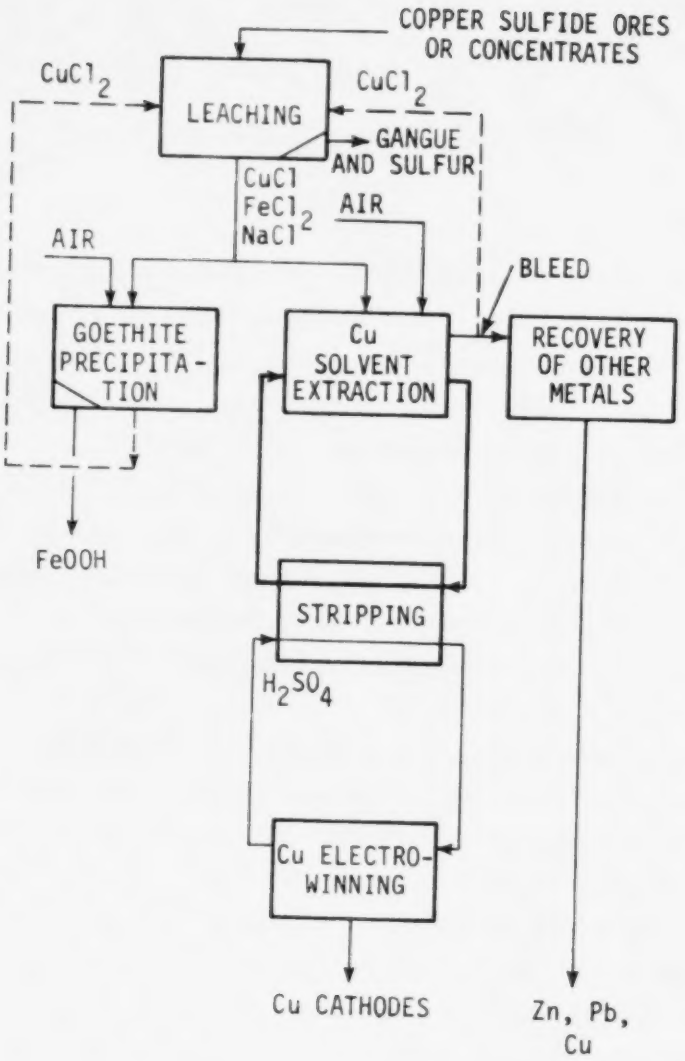

Figure 15. Minemet process for copper.[1]

costs, and the ability to meet antipollution regulations. This process still must be tested on a pilot-plant and semicommercial scale, however, before becoming a viable technique.

This process, like most that include electrowinning, consumes more energy than pyrometallurgical methods.[1]

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3.2 SHERRITT-COMINCO COPPER PROCESS

In conjunction with the Canadian government, Sherritt Gordon Mines, Ltd., and Cominco, Ltd., have developed a hydrometallurgical technique for producing copper from sulfide concentrates. The Sherritt-Cominco (S-C) process is an adaptation of Sherritt Gordon's pressure leaching system for processing nickel concentrates.[1] An integrated 8-Mg/day pilot plant developed for testing the S-C copper process was constructed at Fort Saskatchewan in 1975 and operated in 1976. Results from these tests proved so satisfactory that feasibility studies were conducted on the basic design parameters of a plant in western Canada and one in Arizona. Both would produce 68,000 Mg of copper rod a year from chalcopyrite concentrates. The studies indicate the S-C process could compete with other pyrometallurgical and hydrometallurgical processes.[2,3]

Copper concentrate is pelletized, dried, and fed to Herreshoff-type multiple-hearth roasters. The 690°C temperature in the upper hearths drives off some sulfur from the pellets. The preheated pellets mix with counter-flowing hydrogen gas when they reach the bottom of the roaster, and additional sulfur is removed from the feed as hydrogen sulfide is formed. Some of the sulfur and hydrogen sulfide burns the height of the vessel when air is

introduced to the roaster. As shown in Figure 16, the combustion gases are sent to an acid plant for the production of sulfuric acid.[4]

After leaving the roaster, the activated concentrate is fed to a series of rubber-lined leach tanks containing sulfuric acid. Iron sulfide dissolves in the acid and hydrogen sulfide is liberated. Most of the hydrogen sulfide gas is sent to a small Claus plant to be recovered as elemental sulfur.[4]

The copper-free leach liquor is separated from the solids in a settling tank and undergoes oxidation in a pressurized autoclave. Iron precipitates as jarosite, and sulfuric acid is regenerated.[4]

Residue from the acid leach is subject to high-pressure leaching in a neutral copper sulfate solution. Much of the zinc and remaining iron dissolve and are replaced by copper. After liquid-solid separation, the zinc-rich solution is treated with hydrogen sulfide, which causes zinc sulfide to precipitate. The zinc sulfide is then collected and sold as a byproduct.[4]

The neutral leach residue is treated with recycled acid and oxygen in a two-stage oxidation leach in which copper, residual iron, and zinc are dissolved and elemental sulfur is formed. Over 98 percent of the copper is extracted in the first and second stages of oxidation leaching.[4]

Solid residue from the oxidation leach contains precious metals, molybdenum sulfate (if present in original feed), elemental sulfur, and gangue. Gangue is rejected in a small flotation unit, and sulfur is removed by filtration and solvent extraction. The small quantity of precious metal concentrate left can be sold or processed on site.[4]

Copper solution from oxidation leaching requires further purification before it undergoes electrolysis. Because selenium, tellurium, iron, arsenic, and bismuth would contaminate the final copper or lower efficiency of the electrolysis, these impurities

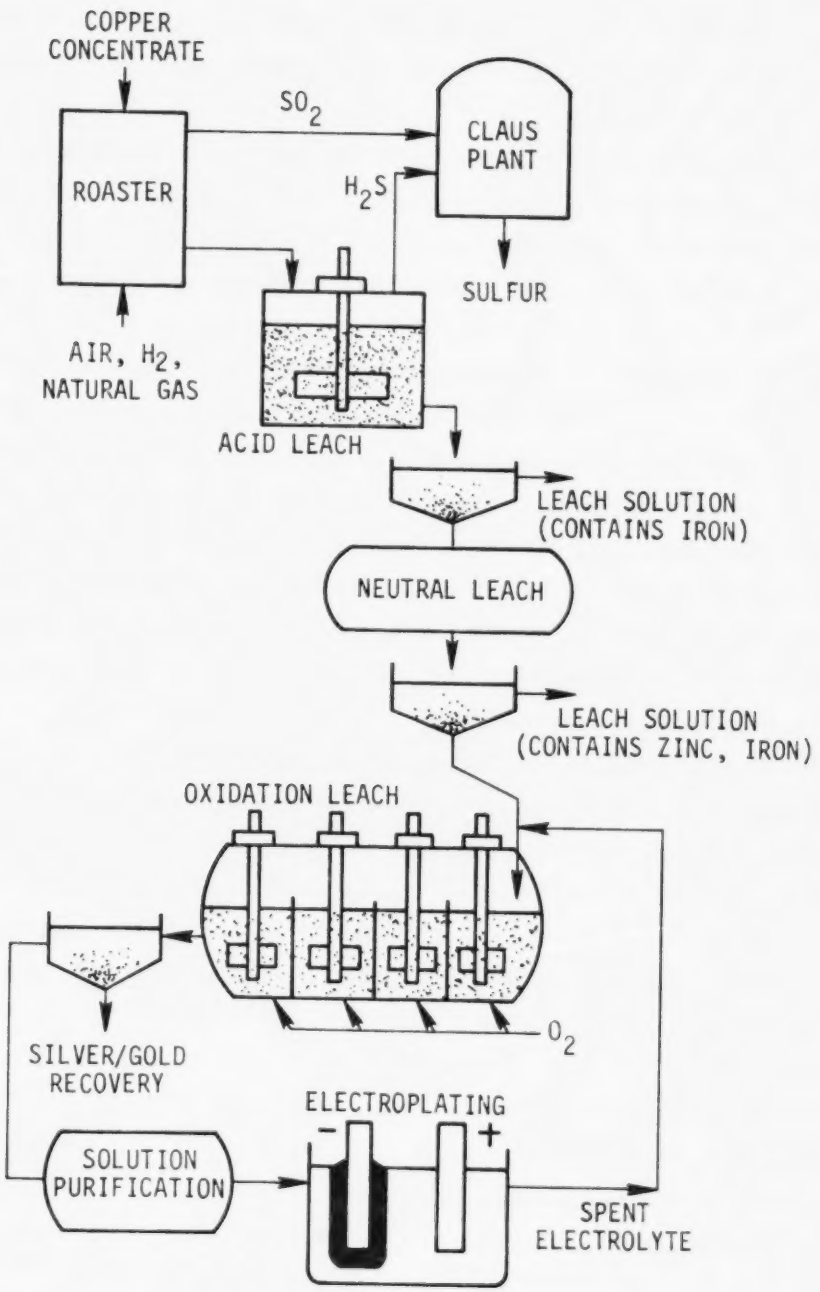

Figure 16. Simplified flowsheet of the S-C process.[4]

are precipitated in a series of high-temperature autoclaves. After pressure filtration, the pure copper solution passes to the electrowinning plant.[4]

The electrowinning plant incorporates many recent design advances, one of which is the use of strippable titanium cathodes instead of starting sheets. Copper is deposited on the cathodes, carefully washed, stripped, and then melted and processed to rod.[4]

Most of the sulfur found in complex sulfide concentrates is processed into elemental sulfur rather than sulfuric acid. This minimizes problems such as meeting emission regulations, transporting acid, and selling the material. Arsenic is removed during purification as stable and insoluble ferric arsenate. Iron precipitated as jarosite is impounded in a lined pond. One problem area may be the production of hydrogen sulfide gas during acid leaching. Another may be the presence of residual elemental sulfur in the waste gangue.[4]

Like other hydrometallurgical copper processes, the S-C copper process consumes more energy than pyrometallurgical processes. The S-C process consumes 92 percent more fossil fuel than a facility utilizing a flash smelting/electrorefining/acid plant process stream;[5] however, in the future, pyrometallurgical facilities may be required to invest more money and energy to dispose of SO_2 as sulfur or neutralized sulfate.

The capital cost of a plant employing the S-C process is purported to be substantially less than that of a comparable flash smelting/electrorefinery, but operating costs are estimated to be slightly higher. Should the flash smelting/refinery be required to add neutralization facilities, however, operating costs of the S-C process would compare favorably.

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3.3 ACETONITRILE EXTRACTION PROCESS[1]

A technique developed in Australia promises energy savings and decreased sulfur dioxide emissions. Original work on the acetonitrile extraction process began at Australian National University; final investigations were made by scientists of the Mineral Chemistry Research Unit at Murdoch University in Perth, Western Australia. The process is capable of recycling scrap copper and refining concentrates faster than conventional methods.

Laboratory experiments have shown that copper can be extracted efficiently by leaching cuprous sulfate solutions from a roasted concentrate by use of the organic chemical acetonitrile. Distillation of the organic produces pure metallic copper powder, thereby eliminating the electrowinning step. Because acetonitrile is decomposed, however, it requires continuous replacement.

Little or no sulfur dioxide and particulates are released into the atmosphere; however, acetonitrile is a poisonous chemical, and widespread use of this process may cause hazardous secondary pollution.

Energy requirements for this process are less than 60 percent of those for conventional processing. The process uses a low-grade waste steam rather than electricity or oil.

Reference

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3.4 LURGI-MITTERBURG PROCESS[1]

In a joint effort, Lurgi Chemi and Huttentechnik, G.m.b.H., of Frankfurt/Main, West Germany; Kupferbau-Mitterburg of Mühlbach, Austria; and the Technical University of West Berlin have developed a pressure acid-leaching system for the recovery of copper values. The process looks particularly attractive for smaller plants and for handling concentrates containing antimony and arsenic, which can cause problems in high temperature processing. A pilot plant treating 3 Mg of concentrate per day in Mühlbach began operating in the spring of 1974 and continued through the first quarter of 1976. The next step will be the construction of a full-scale plant.

Copper concentrates are fed into a vibrational mill for grinding to reduce their size. The grinding also causes a high degree of distortion in crystal lattices, which enhances leaching. The concentrate then is slurried with spent sulfuric-acid electrolyte and pumped into an autoclave, where (at 115°C and an oxygen partial pressure of 10 to 20 atmospheres) the copper dissolves and forms copper sulfate. Following depressurization and discharge from the autoclave, the leach residue, which contains all the iron and sulfur, is thickened and filtered. The filtrate is sent to rubber-lined electrolytic cells for electrowinning of the copper; spent electrolyte is recycled.

Reference

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3.5 PRESSURE-LEACH PROCESS FOR ZINC RECOVERY

Sherritt Gordon Mines, Ltd., and Cominco, Ltd., of Canada are cooperating in the development of an alternative to conventional roast-leach methods of zinc recovery. The new process involves use of a pressure-leach reactor to produce zinc sulfate directly. In 1977, a pilot plant was operated in Fort Saskatchewan, Alberta, and Cominco plans to construct a 64,000-Mg/yr, $20 million commercial unit at its Trail, British Columbia, facility.[1,2]

As illustrated in Figure 17, the feed concentrate at Trail will be split; part will go to the new system and part to the existing roasters. That portion routed to the pressure-leach autoclave will be ground in a wet ball mill to less than 325 mesh before it is combined with recycled sulfuric acid electrolyte in the autoclave. The first autoclave to operate at Trail will be 3.7 m in diameter and 9.1 m long and will consist of a mild steel shell lined with lead and acid brick.[1,2]

Reactions in the autoclave will take place at 150°C and 10.5 kg/cm^2. Zinc sulfide, lead sulfide, and iron sulfide will react to form simple sulfates, elemental sulfur, and water; iron will precipitate as complex sulfate. The slurry will be flashed as it leaves the autoclave and then treated in a flotation unit for sulfur separation. The process stream will then be joined with the conventionally treated concentrate at the acid leaching step for combined treatment in the thickeners and filters.[1]

The pressure-leach system offers certain environmental advantages in that it does not produce SO_2, but rather recovers sulfur in the elemental form. Also, pressure leaching does not form zinc containing residues that require additional treatment.[1]

Cominco estimates that a grass-roots pressure-leach plant offers a 20 to 25 percent capital investment savings, compared with a grass-roots roast-leach plant. This can constitute a $35 million savings for each 64,000-Mg/yr plant. Operating costs should prove to be similar for conventional and pressure-leach operations.[1]

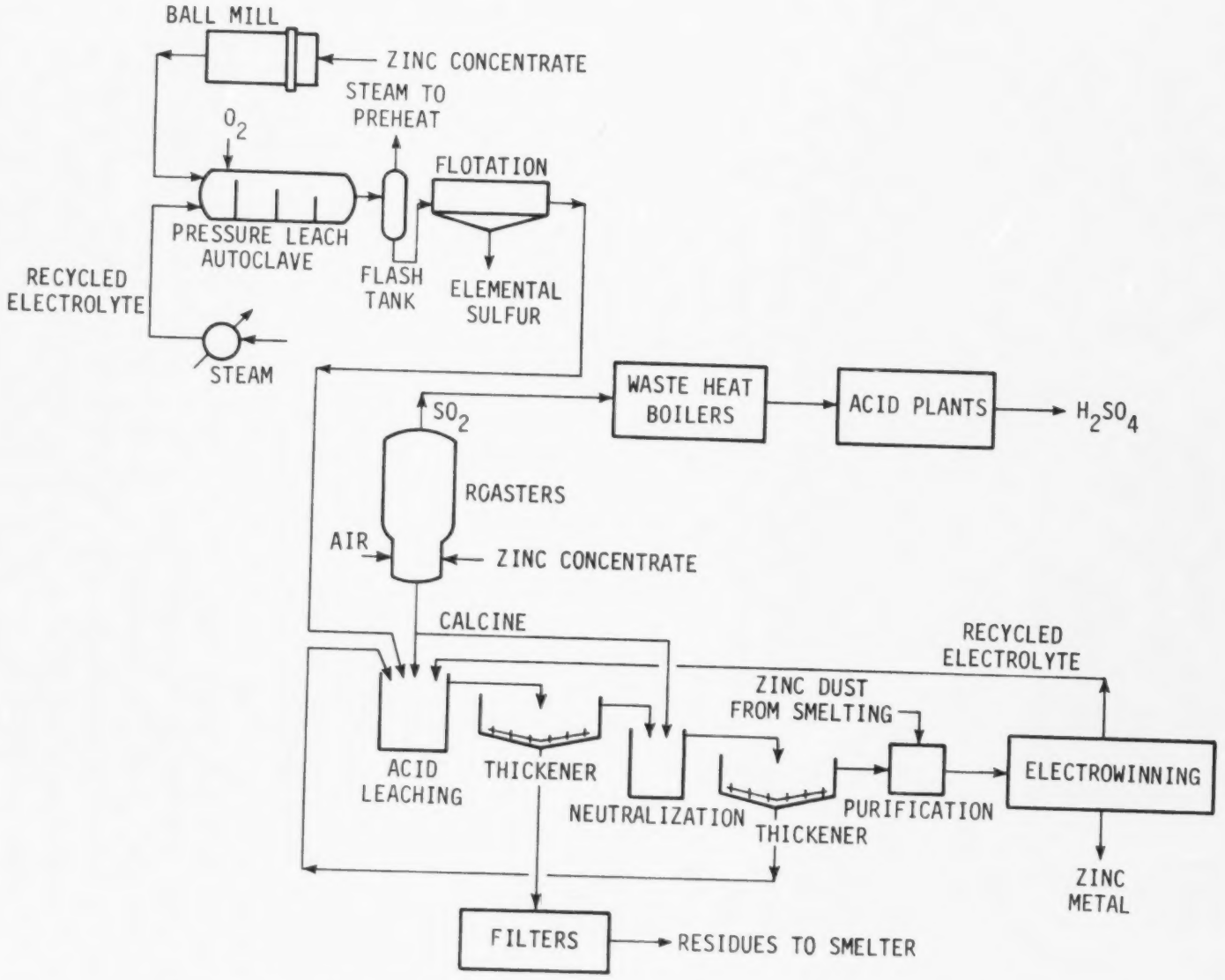

Figure 17. Zinc recovery by pressure-leach autoclave, combined with a conventional plant at Trail, B.C.[1]

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2. Cominco Building Worlds First Zinc Pressure Leaching Plant of 70,000 TPY Capacity. The Northern Miner, April 19, 1978.

3.6 ELECTROLYTIC ZINC PROCESS

The Electrolytic Zinc Company of Australia (EZ) has developed a method for treating oxidized zinc ores, which the New Jersey Zinc Company has modified and piloted with the intention of utilizing it in Thailand. The EZ process is advantageous because oxidized zinc ore is relatively abundant.[1-3]

Figure 18 shows the process flow as piloted by New Jersey Zinc. The ore is ground and then leached with a sulfuric acid/zinc sulfate solution in a series of three large agitated tanks; leaching is continuous. Efficiency of zinc extraction ranges from 90 to 98 percent, depending largely upon the pH in the last leach tank. Neutralization also takes place in a series of three agitated tanks; in this step, dissolved silica and other impurities (e.g., arsenic and iron) are precipitated. Limestone, zinc calcine, or zinc oxide can be used as the neutralizing agent.[1]

After they are neutralized, solids are separated from the zinc solution. This step involves use of a filter of a type yet to be determined; rotary-drum vacuum filters, horizontal-belt vacuum filters, and pressure filters have been tested. Because the leaching of low-grade oxidized ores yields four to five times as much solid residue per unit of zinc as is generated in a conventional electrolytic zinc plant, quick and efficient dewatering of residue is required.[1]

The presence of certain impurities in the neutral filtrate can result in difficulties during electrolysis (as in conventional electrolytic refining). Arsenic, antimony, germanium, nickel, iron, cobalt, copper, and selenium all must be removed

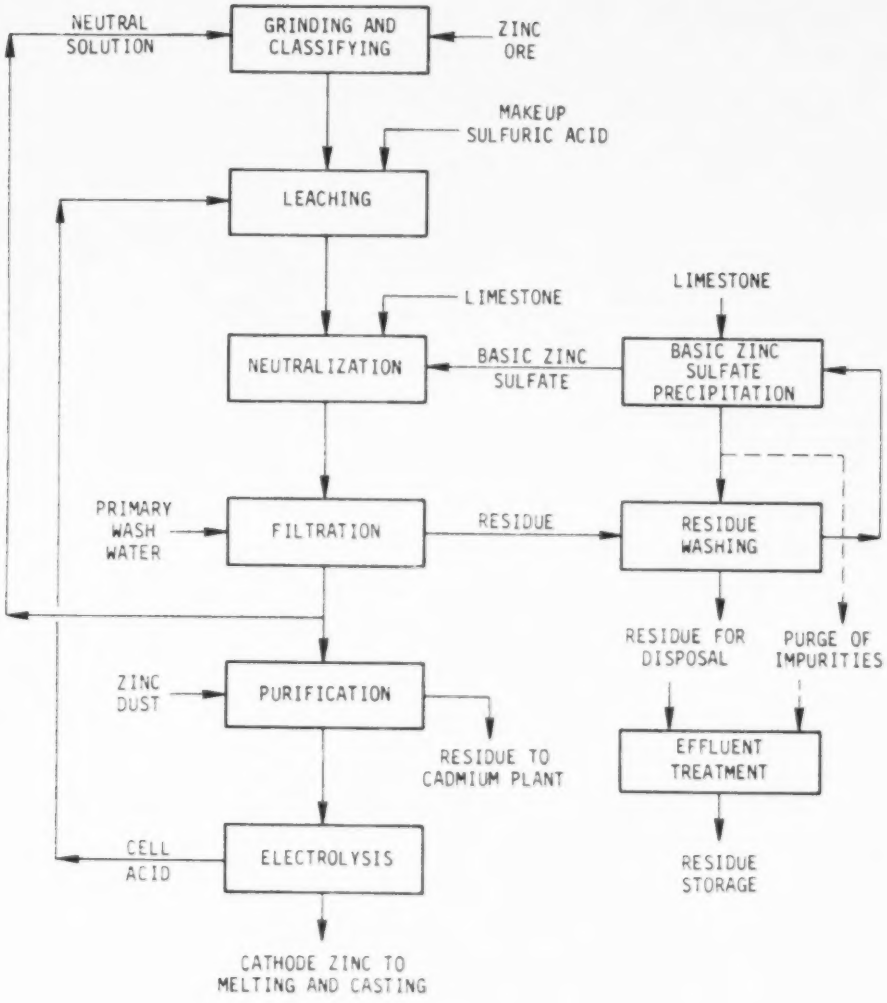

Figure 18. Simplified flowsheet of the EZ process as piloted by the New Jersey Zinc Co.[1]

from the solution. Iron and silica are removed during neutralization, but the others require an additional purification step. Cementation with zinc powder in conjunction with other reagents (such as arsenic, antimony, or copper) is a widely applied technique and the probable method of choice for the EZ process. The purified solution is routed to electrolytic cells for conventional zinc recovery.[1]

As a result of the successful pilot tests, New Jersey Zinc plans a 60,000-Mg/yr plant for Tak, Thailand. This facility is expected to require 4500 kWh electricity per ton of product zinc and an estimated fixed capital (1977) investment of $800 to $1000 per ton of annual zinc capacity ($48 to $60 million).[1]

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3.7 OTHER TECHNIQUES FOR TREATING OXIDIZED ZINC ORES

Oxidized zinc ores have been used in the production of zinc metal since the industry's development. At one time they were the major component of zinc smelter feed, however, their use has declined because of the inability of electrolytic plants to process them satisfactorily. Oxidized ores contain significant amounts of zinc silicates, which dissolve in sulfuric acid to form silicic acids and colloidal silica. These compounds gel and interfere in the separation of zinc liquor from residue solids. Nevertheless, the large amount of oxidized ore throughout the world and the ease with which it can be mined have encouraged the development of several processing techniques.[1]

The Radino process was patented in the United States in 1959 as a method for treating a Brazilian zinc silicate ore. This process utilizes a lengthy leaching cycle and numerous additions of aluminum sulfate to flocculate the silica and render it filterable.[1-3]

The "Italian" process (developed by F. Sciacca and patented in Brazil in 1963) is another process for treating Brazilian zinc silicate ores. In this process, leaching is carried out in autoclaves at elevated temperatures to form a granular colloidal silica.[1]

The Vielle-Montagne process incorporates a series of leaching vessels in which the acidity is progressively increased at temperatures between 70° and 90°C. The operation lasts 8 to 10 hours and results in the silica precipitating in a crystalline form. The process was patented in the United States in 1976.[4]

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3.8 HYDROCHLORIC ACID LEACHING OF FABRIC FILTER DUST[1]

Australian researchers have developed a procedure for recovering metal values from copper smelter fume. The Electrolytic Refining and Smelting Company of Australia Pty., Ltd., sold all of its Port Kembla fabric filter dust to Hardman Chemical Pty., Ltd., for processing. The dust, valued in excess of $1 million 1977 Australian dollars a year, was leached with sulfuric acid to obtain an easily purified zinc sulfate solution, and the leach residue was resold. Declining profitability of the operation eventually induced Hardman, along with the Mineral Chemistry Research Unit of Murdoch University, to investigate the possibility of further treating the residue. Results of their investigation led to the hydrometallurgical technique described below.

After the copper smelter fabric filter dust is leached with excess sulfuric acid and about 65 percent of the zinc is recovered as zinc sulfate, the solid residue is leached twice with hydrochloric acid. This brings into solution more than 90 percent of the major metals, excluding lead. Hot-water washing of the residue following the acid leach precipitates about 75 percent of the lead as lead chloride.

By proceeding in a stepwise progression, the technique precipitates most of the metal fractions contained in solution. The end products include zinc sulfate, zinc chloride, cadmium, copper, tin, bismuth, and lead chloride. This dissolution, classification, and recovery process is similar to methods used in the processing of electrolytic zinc.

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SECTION 4

ELECTROLYTIC PROCESSES

4.1 FLUIDIZED-BED ELECTROLYSIS[1]

Akzo Zout Chemie of the Netherlands has developed an electrolytic process for the removal of low concentrations of metals from process or waste streams with high flow rates. The technique makes use of a closed fluidized-bed electrolytic (FBE) cell. Possible applications include separation and winning of metals in hydrometallurgical processes, treatment of liquid waste streams before discharge, and electrolyte purification at an electrolytic zinc plant.

As shown in Figure 19, an FBE cell consists of two compartments separated by a diaphragm; these contain the anode and cathode. In the cathode compartment, metal particles are fluidized by the waste or process stream, and additional metal particles (about 0.5 mm in diameter) are added. As the electrolysis results in deposition of the waste or process metal upon the added metal particles, they increase in size to about 1 mm and sink to the bottom of the cell, where they are recovered.

The system can be easily expanded by the installation of many diaphragms in one cathode compartment; thus only one catholyte supply is required. The anodes are placed in the center of the diaphragms. Because the diaphragms are relatively impermeable, the anolyte and catholyte streams remain segregated. This segregation can be ensured by pressurizing the anode compartment to prevent inward seepage by the catholyte. Recirculation of the catholyte is necessary for maintenance of fluidization velocity even when the feed supply is variable.

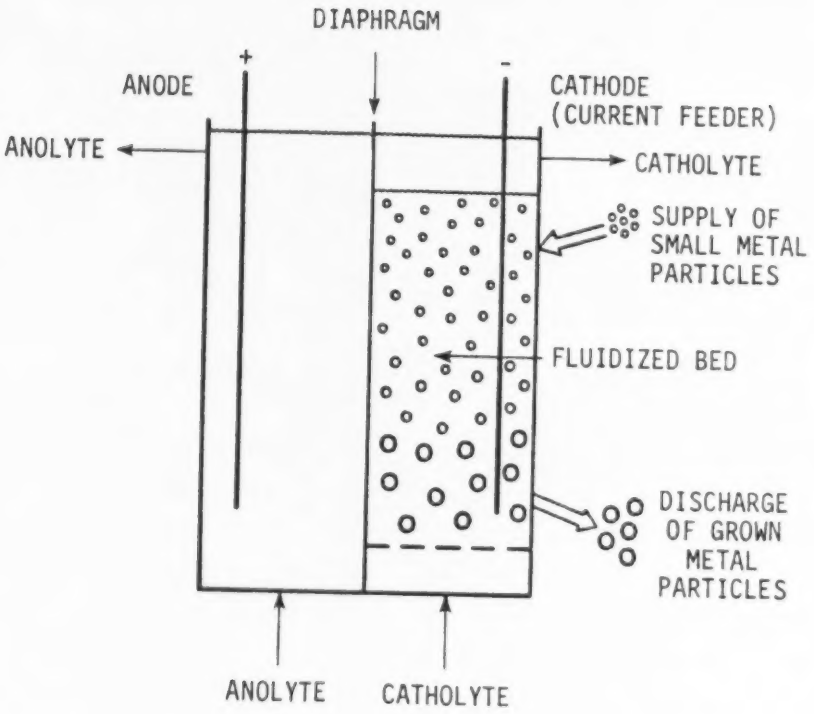

Figure 19. Schematic view of an FBE cell.[1]

An Akzo test of FBE in the treatment of copper-containing wastewater lowered the copper content from 100 mg/liter to less than 1 mg/liter in one pass. In another test, involving the removal of mercury from the brine stream of a mercury-cell, chlor-alkali electrolysis plant, the mercury content of the brine was reduced from 5 mg/liter to about 0.05 mg/liter. Ionic and metallic mercury deposited on copper particles, which were recovered by distillation of the amalgamated particles.

Other applications have included separation of copper and nickel in a nickel electrolyte and removal of copper and cadmium from a zinc electrolyte. Use of FBE in the latter application has been reported to be very attractive economically.

A cost comparison between FBE and zinc dust cementation for electrolyte treatment at a 136,000-Mg/yr electrolytic zinc plant reportedly indicates that the net operating profit achievable with FBE is $2.8 million per year higher as a result of an extra yield of 4500 Mg/yr of pure copper and 14 Mg/yr of cadmium. Capital investment should be $2 million lower for FBE, but energy requirements and thus operating costs are expected to be higher.

Reference

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4.2 DEXTEC PROCESS[1]

Dextec Metallurgical Pty., Ltd., of Australia is joining with China to develop a new copper production process called Dextec. Reportedly, this process is capable of producing copper metal from concentrates without the use of a smelter and at a cost 25 percent below those involved with conventional techniques. The method converts ore to metal in one step, at atmospheric pressure, through use of an electrolytic diaphragm cell. It also recovers elemental sulfur, thus avoiding SO_2 air emissions. The technique may prove applicable to other metals as well.

The Peking Institute of Mining and Metallurgy will build a pilot plant to test the technique at commercial levels. Should these tests prove successful, the Chinese will be granted free use of the process, although Dextec will retain the patents and marketing rights.

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4.3 CATHODE SHEET STRIPPING[1]

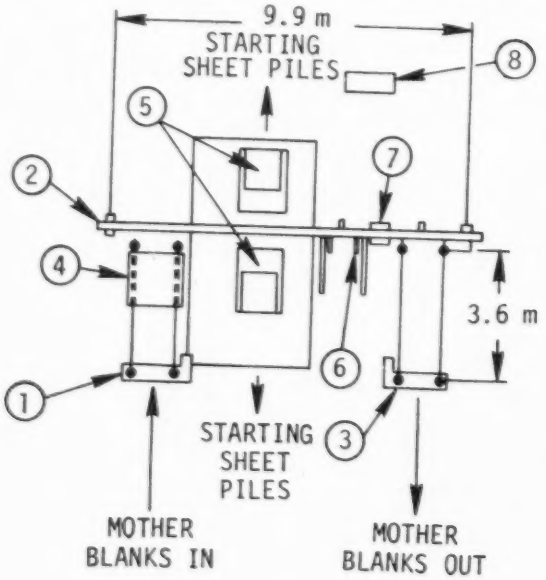
Outokumpu Oy has developed a mechanized method of stripping starter sheets for electrolytic refining from copper mother blanks (starter blanks). Mechanized stripping operations were begun at Outokumpu's Pori, Finland, refinery in the spring of 1974 in an effort to reduce labor and operating costs.

The system consists of three conveyors and a stripping machine and occupies about 85 m^2. The stripping machine is capable of stripping one pair of sheets in 8 seconds and can handle 900 starter sheets per hour at peak capacity. Although designed for copper, the machine could easily be modified for stripping zinc and nickel.

As shown in Figure 20, mother blanks are fed into Conveyor 1 and transferred to the washing unit. The blanks then connect with Conveyor 2 and pass in vertical single file through the stripping station.

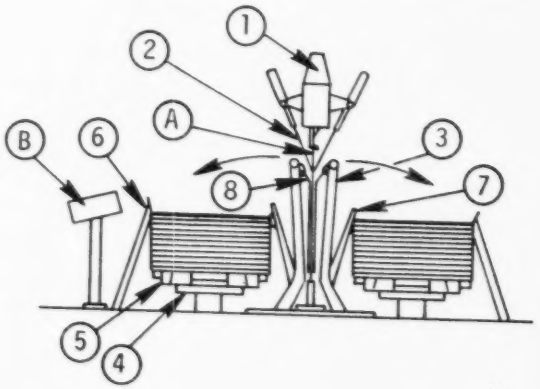
A mother blank is locked into position during stripping so that blades may open the upper edges of the sheet and pneumatically operated jaws on both sides of the sheet may grasp the opened upper edges. Copper sheets are peeled from the mother blanks and placed on adjustable hydraulic tables. Stripped mother blanks are then coated with a chemical and collected on Conveyor 3, where they are positioned with the required spacing for the stripper cells.

GENERAL LAYOUT OF STRIPPING MACHINE
FOR COPPER CATHODE STARTER SHEETS



1. CONVEYOR 1
2. CONVEYOR 2
3. CONVEYOR 3
4. WASHING UNIT
5. STRIPPING STATION
6. MAINTENANCE TRACK
7. SPRAY COATING UNIT
8. CONTROL DESK

VERTICAL SECTION OF STRIPPING SECTION



A. MOTHER BLANK
B. STARTING SHEET
1. STRIPPING CONVEYOR
2. STRIPPING BLADE
3. GRIPPING JAW
4. ADJUSTABLE HYDRAULIC TABLE
5. PALLET
6. PIE STRAIGHTENER
7. GUIDE BEAM
8. CONTROL DESK

Figure 20. Cathode sheet stripping.[1]

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SECTION 5

AIR POLLUTION CONTROL PROCESSES

5.1 DOWA BASIC ALUMINUM SULFATE PROCESS

Dowa Mining of Japan has developed a process for weak-stream SO_2 removal that utilizes a basic aluminum sulfate solution as the absorbent. Four Japanese nonferrous facilities use this process to treat acid plant tail gases; its application at Dowa's double-contact sulfuric acid plant in Okayama is described.[1-4]

At 80°C, tail gas from the acid plant contains 600 ppm SO_2 and 50 ppm SO_3 and is produced at a rate of 140,000 Nm^3/h. As shown in Figure 21 the gas is routed to the lower end of an absorbing tower, where it is contacted countercurrently by a downward spray of basic aluminum sulfate absorbent, which absorbs the SO_2. The solution then flows to an oxidizing tower, where fine air bubbles are injected to oxidize the sulfite to sulfate. After a brief retention time, most of the absorbent is recycled to the absorption tower, but a small portion is sent to a tank for neutralization with limestone. The neutralized slurry overflows to a thickener, where gypsum crystals precipitate; thickener underflow is routed to a centrifuge where gypsum is filtered, washed, and discharged. Thickener overflow, filtrate, and wash water are recycled to the absorption tower.[1-3]

Treated gas passes through a mist eliminator and then exits through a stack. Concentration of SO_2 is reportedly 10 to 15 ppm.[1-3]

Absorption of SO_2 is increased with higher aluminum concentrations and basicity and lower temperatures. In commercial operation, basicity should be lower than 40 percent to prevent

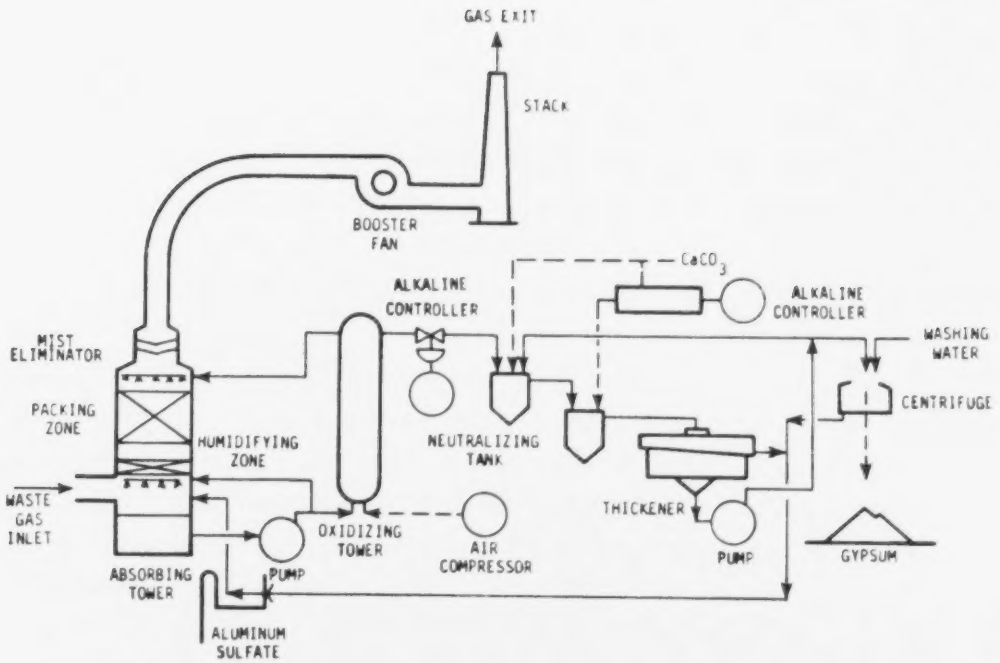

Figure 21. Dowa basic aluminum sulfate process.[1]

aluminum precipitation and plugging in the absorption tower. Basicity is defined as the degree of neutralization of aluminum sulfate solution and may be quantified as follows:

$Al_2(SO_4)_3$	Basicity = 0%
$Al_2(SO_4)_3 \cdot Al_2O_3$	Basicity = 50%
$Al(OH)_3$	Basicity = 100%

Because of incomplete washing, some aluminum is lost--about 0.5 kg per metric ton of gypsum.[1-3]

Direct operating costs (1976) are estimated to be $3.00 per 10,000 Nm^3 of input gas; this figure excludes labor costs. Typical operating requirements are 0.81 Mg $CaCO_3$/h, 15 kg $Al_2(SO_4)_3$ (Al_2O_3 8%)/h, 7 H_2O/h, and 65 kWh electricity/10,000 Nm^3 tail gas.[1-3]

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5.2 MITSUBISHI LIME/LIMESTONE PROCESS

Mitsubishi Metals Company of Japan has developed a system of SO_2 control utilizing lime as a nonregenerative absorbent. The development stage lasted about 20 years, and the process is now in operation at Mitsubishi's Onahama smelter.[1-5]

The reverberatory furnace gas stream contains an average of 2.4 percent SO_2. At full capacity, the furnaces discharge a gas stream of about 3120 Nm^3/min. It is reported that the FGD system is capable of lowering the SO_2 content of the gas stream to below 100 ppm before it is discharged.

Flue gas from the Onahama reverberatory furnace passes through waste heat boilers and Cottrells, as shown in Figure 22. It then enters a horizontal wash tower. The sprays and internal baffles in this cylindrical tower lower the gas temperature to 60°C. Gas temperature is reduced further in the five heat exchangers immediately downstream of the wash tower.[1-3,6,7]

At this point, the gas stream can be split, with part going to an MgO system and part to the lime system. Currently, the poor demand for sulfuric acid dictates full flow to the lime/limestone system, where SO_2 is removed by two absorber towers set in series. A lime slurry is sprayed from the top of the towers and the absorbent flow rate through the first absorber is about half that in the second absorber.[1] Approximately half the SO_2 is absorbed in each tower.

Because some absorbent is entrained in the gas stream, a mist eliminator is located downstream of the towers. The gas stream passes through a blower and an electrostatic precipitator before it is emitted through the stack.[1]

The pH of the calcium sulfite slurry at the bottom of the first absorber tower is between 4 and 5; the slurry is first pumped to a pH adjuster, where the pH is lowered to between 3 and 4 with sulfuric acid. It then passes (at a rate of about 200 m^3/h) to three oxidation towers, where it is mixed with compressed air. Most of the gypsum slurry flows from the oxidizing towers to a thickener, but about 20 percent goes to the lime tank to supply seed crystals. The crystals later enter the absorption system in the second tower to help prevent deposition on absorber surfaces.[1]

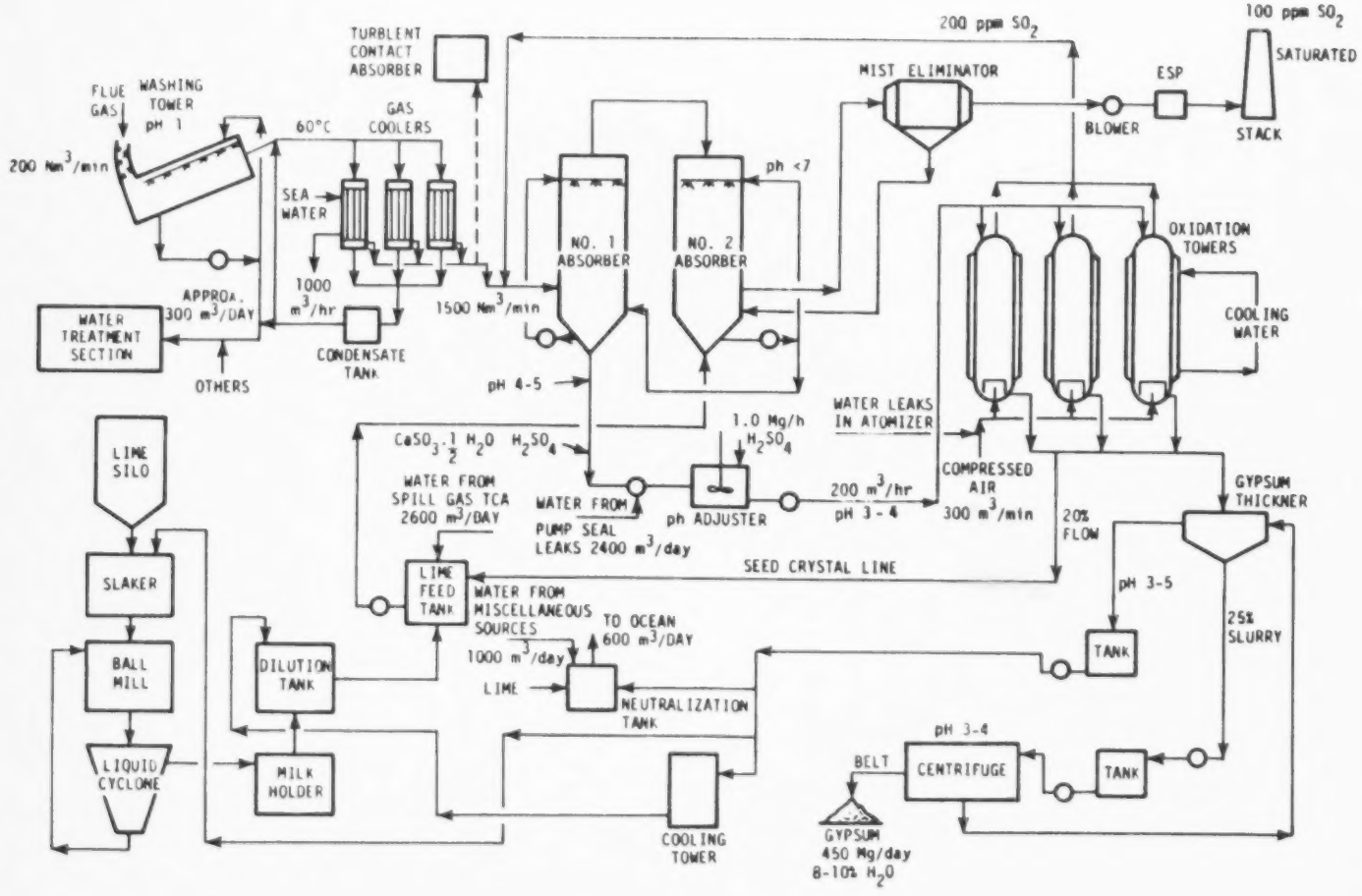

Figure 22. Mitsubishi lime/limestone process used at Onahama.[7]

Underflow from the thickener is a 25 percent slurry. This slurry is routed to a bank of 14 centrifuges where solid gypsum is separated at a rate of 450 Mg/day. The H_2O content of the slurry is 8 to 10 percent. The liquid is recycled to the thickener. Thickener overflow is routed to the slaking system, where it is used for diluting the slaked lime. Excess water from the thickener overflow is neutralized and discharged.[1]

The slaked lime passes to a ball mill and liquid cyclone. The heavy material from the liquid cyclone is recycled to the ball mill, and the light material (calcium hydroxide or lime milk) is sent to the milk holder and dilution tank. From the dilution tank, the milk goes to the lime feed tank and back to the second absorber.[1]

Versions of this process are in use on coal-fired generators in the United States, but these domestic applications do not make use of compressed air in the oxidation phase.

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5.3 MAGNESIUM OXIDE PROCESS[1,2]

The magnesium oxide SO_2 concentration system was developed by Mitsubishi Metals in conjunction with Tsukishima Kikai Company over a period of about 3 years (1969 to 1971). Full-scale operation at Mitsubishi's Onahama smelter began in 1973.

Initial treatment of the furnace off-gas is the same as for the lime/limestone process, with the two systems sharing the waste heat boilers, Cottrells, horizontal wash tower, and five heat exchangers. During this treatment gas temperatures are reduced to about 45°C. The gases routed to the MgO system are then passed through a turbulent contact absorber (TCA), where they are contacted by a countercurrent flow of magnesium hydroxide slurry. Magnesium sulfite and some magnesium sulfate are formed in this stage.

The absorbent containing the magnesium sulfate is passed to a liquid cyclone, where it is rough cut to a slurry of 40 tc 50 percent solids. Overflow from the cyclone is filtered and combined with the recovered MgO; the high-solids underflow is treated in centrifuges for further removal of liquid. Collected liquid is filtered and recycled.

The centrifuged magnesium sulfite is sent to two indirect rotary steam-heated dryers, and is then combined with coke and treated in a rotary calciner. The calciner breaks down magnesium sulfite to SO_2 and MgO. The SO_2 is routed to an acid plant. The MgO is sent to a slaker, where it is mixed with

overflow from the centrifuge and cyclone systems; the resulting magnesium hydroxide is then either further processed by a tube or ball mill or returned directly to a storage tank before it is recycled. The storage tank also receives makeup magnesium hydroxide.

In 1977, the capital cost of the 88,000-Nm^3/h system at Onahama was estimated to be $2.5 million. A breakdown of annual operating costs indicates the following: MgO, $500,000; bunker C fuel, $400,000; coke, $10,000; steam, $200,000; water, $100,000; and labor, $400,000. Total operating cost is probably around $2 million.

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5.4 BOLIDEN COLD SEAWATER PROCESS

Since 1970, Boliden a.-b. of Sweden has been utilizing cold seawater to scrub SO_2 from the combined gas stream at its Rönnskär works. The combined stream is a blend of gases from an electric copper furnace, multiple hearth furnaces, converters, and a lead smelter. Two commercial-scale plants are in operation at Rönnskär; the older plant (1970) has an SO_2 capacity of 5 Mg/h, and the new plant (1976) has an SO_2 capacity of 15 Mg/h.[1,2]

The combined gas stream has a flow rate of 60,000 to 70,000 m^3/h at about 150°C; SO_2 concentration ranges from 0.5 to 5 percent and averages 3 percent. As shown in Figure 23, after

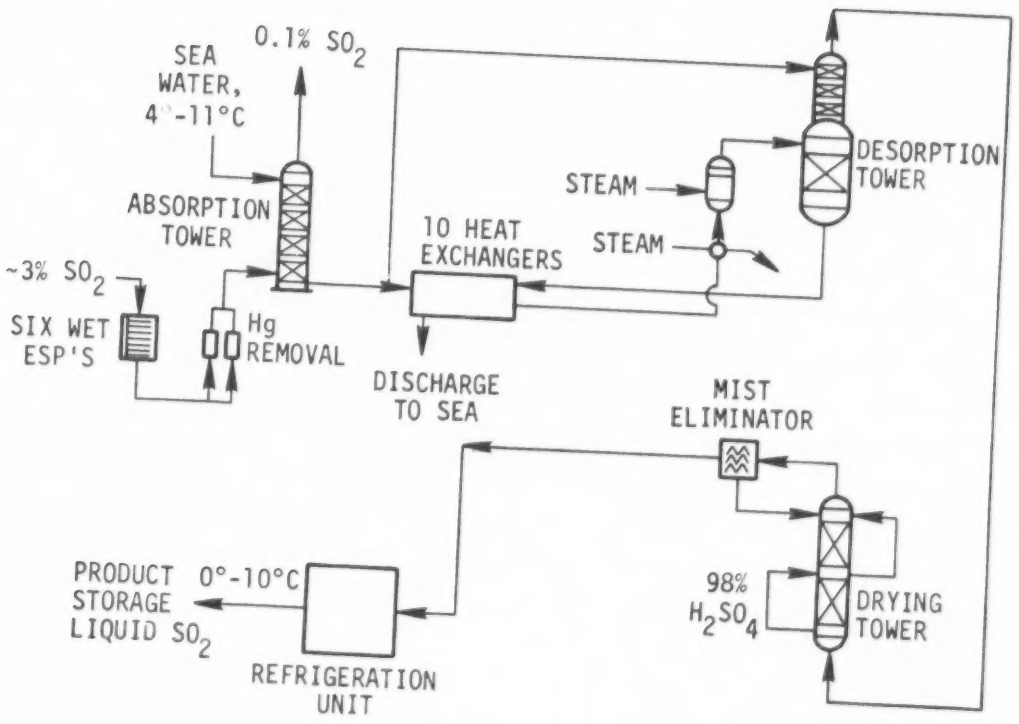

Figure 23. Boliden cold seawater process.[4]

the gas has been cleaned in wet electrostatic precipitators and treated for mercury removal, it is routed to the absorption tower where the SO_2 is absorbed in the cold (4° to 11°C) seawater.[3] At this operating temperature, the solubility of SO_2 in water is about 12 g/liter. The treated gas contains 0.1 percent SO_2 or less.[1-4]

Seawater from the absorber is heated to 60°C by injection of low-pressure steam; it then enters a vacuum desorption tower that operates at a pressure of 20 kPa absolute. The SO_2 is released in the desorption tower and is cooled to between 12° and 15°C by a slipstream from the absorption tower. The stripped seawater is cooled and discharged to the sea.[2,4]

After cooling, the SO_2 gas is dried by contact with sulfuric acid, and the pressure is raised slightly to avoid freezing in the refrigeration unit. The gas is further cooled and compressed; this results in its liquefication. The liquid SO_2 is stored at a temperature of between 0° and 10°C.[4]

This process offers advantages in that a wide range of SO_2 concentrations can be treated with high removal efficiencies and without scaling problems. The availability of cold seawater is extremely limited in geographic range, however, and discharged water may contain high levels of sulfite.[4]

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5.5 FLAKT-BOLIDEN CITRATE PROCESS

Boliden a.-b. of Sweden, in conjunction with the Norwegian Technical Institute (SINTEF) and Svenska Flaktfabriken (Flakt), has developed a variation of the cold seawater SO_2 scrubbing process that can be used where cold seawater is not available. The success of the process results from the discovery that the addition of weak bases having good buffering properties to water increases the SO_2 absorption capacity. In the pilot-scale plant at Boliden's Rönnskär works, a combination of citric acid and sodium citrate is used because it has a low vapor pressure and is chemically stable. The absorption section of the process is similar to the Bureau of Mines citrate process.[1-3]

The pilot plant, which began operation in September 1976, cleans approximately 5000 Nm^3/h of off-gases from various smelting processes. The SO_2 concentration varies from 0.2 to 6 percent; however, typical operation is 3 percent SO_2. For a 3 percent SO_2 off-gas stream, the steam consumption is 2 kg steam/kg SO_2 removed, and the oxidation rate is 0.1 percent of the absorbed SO_2. The gas stream is cleaned of particulate, cooled by direct water injection, and passed through a mist eliminator before it enters the absorption tower. The gas temperature at the absorber inlet is between 45° and 65°C. The absorber operates at atmospheric pressure and gas/absorbent contact is countercurrent; absorption efficiency is between 90 and 99 percent. The cleaned gas is passed through a mist eliminator and exits through a stack to the atmosphere.[1-3,4]

As shown in Figure 24, the absorbent is pumped from the bottom of the absorber tower to the top of the stripping tower, where stripping is accomplished by countercurrent steam treatment. Low-pressure steam is introduced at the bottom of the stripping tower, and the tower is kept under vacuum. This treatment produces a mixture of SO_2 and water vapor. The absorbent is recirculated to the absorber tower.[1,4]

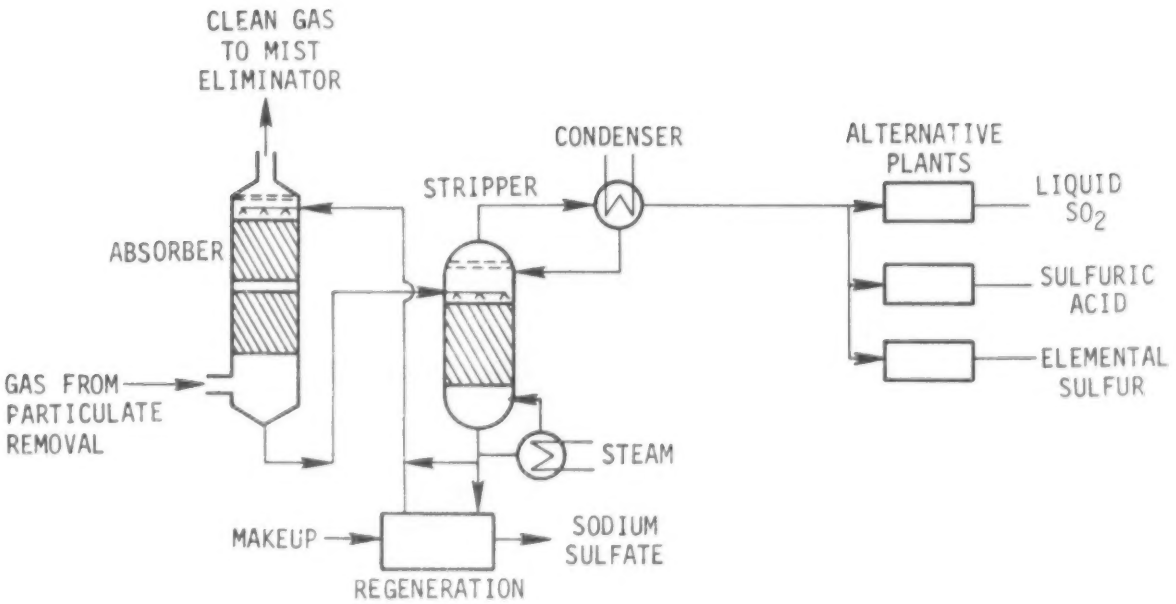

Figure 24. Flakt-Boliden citrate process.[2]

The mixture of SO_2 and water from the stripping column is cooled in a condenser, which separates most of the water from the mixture. The condensate, which contains only a small quantity of SO_2, is returned to the stripping tower. The concentrated SO_2 stream can be routed directly to a Claus plant for production of elemental sulfur or to a contact plant for sulfuric acid production, or it can be condensed by refrigeration to liquid SO_2. If liquid SO_2 is produced, the water remaining in the gas first must be removed by contact with concentrated sulfuric acid in a small packed tower.[1,4]

After drying, the SO_2 gas still contains some inert gas. The dried SO_2 gas is conveyed to a Freon cooler for condensation, and the liquid SO_2 is stored under pressure. The tail gas is returned to the absorber.[1,4]

Some sodium sulfate may form in the absorbent and must be removed. Sulfate levels can be kept acceptable by regeneration of an intermittent or continuous bleed-off from the stripper of about 1 percent of the stripped absorbent. Seed crystals and a cooling unit are used to recover sodium citrate and remove sodium sulfate.[2]

Application to a 1.5 percent SO_2 gas stream of 157,700 Nm^3/h would require approximately 325 kW and about 30,000 kg/h of low-grade steam.[1]

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2. Coleman, R.T., Jr. Emerging Technology in the Primary Copper Industry. Prepared for the U.S. Environmental Protection Agency under Contract No. 68-02-2608. Radian Corporation, Austin Texas, August 1978.

3. Matthews, J.C., et al. SO_2 Control Processes for Nonferrous Smelters. EPA 600/2-76-008, January 1976.

4. The Flakt-Boliden Process for SO_2 Recovery. AB Svenska Flaktfabriken, 1977.

5.6 SHOWA DENKO PROCESS

Showa Denko K.K. of Japan has developed a double alkali process for SO_2 removal, which can be applied to acid plant tail gases and other weak SO_2 streams. At the time of development, declining demand for sodium sulfite and increasing marketability of gypsum in Japan combined to make this process economically advantageous in comparison with sodium processes. The process is in use at Nippon Mining's copper-lead smelter at Saganoseki, Japan.[1]

At Saganoseki, exhaust gases from the single-contact sulfuric acid plants, which contain 1500 to 2000 ppm SO_2, are treated in the Showa Denko scrubber.[1] Principal chemical reactions involved in this process are:

(1) $NaSO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3$

(2) $2NaHSO_3 + CaCO_3 \rightarrow Na_2SO_3 + CaSO_3 \cdot 1/2\ H_2O + CO_2 + 1/2\ H_2O$

(3) $2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$

(4) $Na_2SO_4 + CaSO_3 \cdot 1/2\ H_2O + H_2SO_4 + 3H_2O \rightarrow 2NaHSO_3 + 2CaSO_4 \cdot 2H_2O$

(5) $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$

The weak SO_2 stream enters a venturi and flows upward into a separator. The absorbent, consisting of Na_2SO_3, $NaHSO_3$, and $NaHSO_4$, is injected into the venturi throat and is entrained in the upward gas flow. When the gas flow rate declines in the separator section, the absorbent drops out of suspension.[1]

Following absorption of the SO_2 (Reaction 1) and deentrainment, part of the absorbent solution is neutralized with limestone or lime (Reaction 2) and forms a calcium sulfate slurry. This slurry is filtered, and the filter cake is reslurried. Sulfuric acid is added to reduce the pH of the filter cake slurry (Reaction 4). The slurry is then oxidized with air to form calcium sulfate, which crystallizes as gypsum. The gypsum crystals are dehydrated in a centrifuge.[1]

The addition of sulfuric acid to the filter cake slurry promotes gypsum precipitation and minimizes loss of sodium. The pH of the absorbent is maintained with caustic and filtrate (Reaction 5). (Minimizing sodium loss lessens the need for caustic.) Concentration of SO_2 in gases leaving the Showa Denko system is between 50 and 100 ppm.[1]

Versions of this process are in use in the United States, but not for treatment of weak streams at nonferrous smelters.[2]

References

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5.7 ZINC OXIDE PROCESS

Mitsui Mining and Smelting Company, Ltd., of Japan has developed a zinc oxide process for SO_2 removal from acid plant tail gas at its Hikoshima zinc smelter.[1,2]

Tail gas from the single-contact acid plants contains 0.15 to 0.18 percent SO_2. This gas is routed to an absorber tower where it contacts a countercurrent stream of zinc oxide and water. Zinc calcine or crude zinc oxide is slurried with acid plant drainage and some other industrial effluents to make up the absorbent solution.[1]

Over 97 percent of the SO_2 is absorbed; the absorbent is then sent to a tank for decomposition with either heat or sulfuric acid. The Hikoshima smelter is reportedly using acid decomposition at present; temperature is 85° to 90°C and zinc sulfate and water are produced. The SO_2 content at discharge is 30 ppm or less and the gas is cleaned further in a wet ESP.[1,2]

A gas volume of 480 Nm^3/min is treated. Figure 25 is a simplified flow diagram.[1]

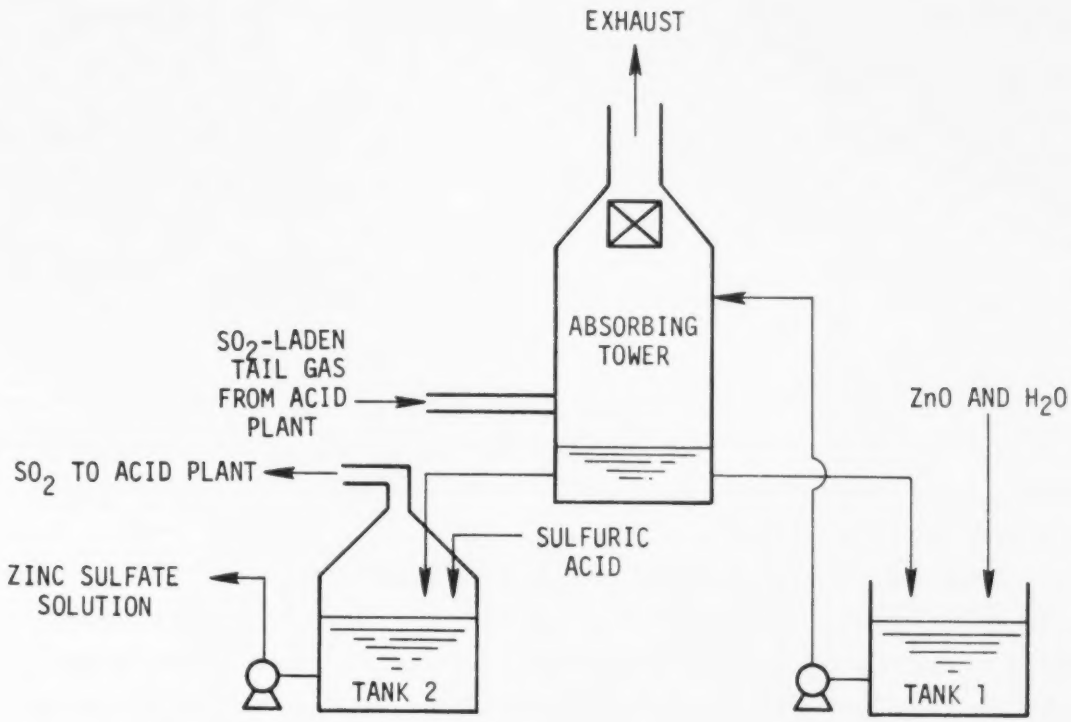

Figure 25. Zinc oxide process.[1]

This process is advantageous in that the zinc sulfate solution may be treated in electrolytic cells for zinc recovery. A weak stream of sulfuric acid or soluble sulfates is produced, however, and therefore constitutes a potential source of water pollution.[1,2]

References

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5.8 FLASH AGGLOMERATION

The smelting of lead-containing scrap materials such as storage batteries generates a dust rich in lead oxides; however, this dust also consists of oxides of other metals together with chlorides, sulfides, and sulfates. At most secondary lead smelters, this flue dust is directly recycled to the blast furnace. This practice leads to dust losses; degradation of the dust also occurs because the lead chloride present in the dust is more volatile than the other material in the furnace, and recirculation of the dust tends to "distill" the chloride. Agglomeration of the captured dust and the addition of fluxes allow the melting point of the dust to be adjusted so it melts lower in the furnace shaft; the chloride is then fixed in the slag. Paul Bergsøe and Son A/S of Denmark have devised a system of accomplishing this agglomeration in an efficient manner.[1-6]

As indicated in Figure 26, dust from fabric filter hoppers is fed via screw conveyor to an agglomeration furnace. A flux such as sodium carbonate or borax may be added to the dust while it is on the conveyor. Upon landing on a sloped hearth within the furnace, the dust is melted by an impinging flame. The molten material flows down the hearth, out a tap hole, and into a

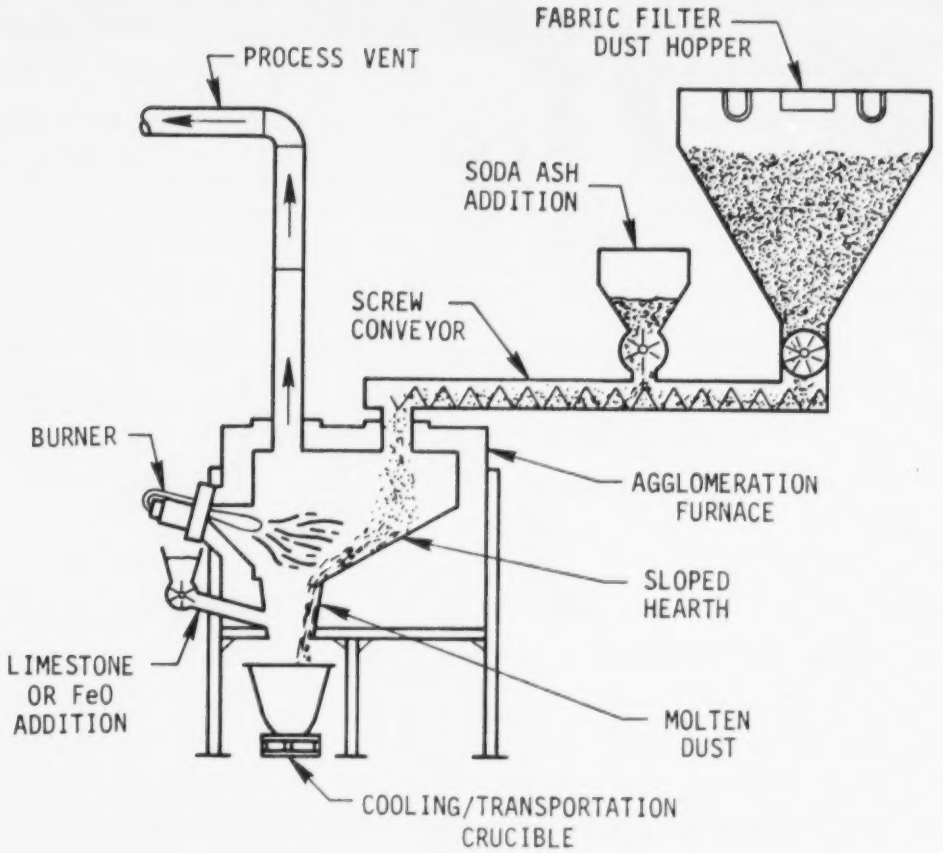

Figure 26. Flash agglomeration furnace.[1]

waiting cooling/transportation crucible. The solidified material is later broken into suitably sized chunks, mixed with coke and flux, and charged to the blast furnace along with batteries or scrap.[1-3]

Flue dust agglomeration decreases the volume of material being returned to the blast furnace by about 80 percent; thus additional batteries or scrap may be charged. Since the recycle stream is reduced from 10 percent of the charge to about 2 percent, an increased furnace throughput of 8 percent is theoretically possible. For a 23,000-Mg/yr smelter, realization of one half this increase in throughput has been calculated to constitute a $66,120 per year (1977) increase in gross revenues. The cost of the flash agglomeration has been estimated to be less than $100,000 (1977) installed. In addition, both stack and fugitive dust emissions are reduced.[1-3]

The agglomeration furnace is oil fired and consumes 24.6 liters of oil per hour.[2,4]

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2. Mackey, T.S., et al. Flash Agglomeration of Flue Dust. J. Metals, 29(11):12-15, November 1977.

3. U.S. Patent Office. Method for Treating Flue Dust Containing Lead. Patent No. 4,013,456 issued to Svend Bergsøe, March 22, 1977.

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5. Mackey, T.S., et al. Smelting of Unbroken Batteries. American Institute of Mining, Metallurgical, and Petroleum Engineers, 106th Annual Meeting, Atlanta, Georgia, March 9, 1977.

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5.9 BOLIDEN DRY SELENIUM FILTER

Boliden a.-b. of Sweden has developed a process that uses a selenium-impregnated filter to remove mercury as mercuric selenide (HgSe) from roaster gases at nonferrous smelters.[1-4]

The gases are cleaned of particulate and dried prior to entering an absorption reactor tower. The tower is closed at the top so that gases entering the bottom diffuse radially through a cylindrical filter consisting of an inert porous material that has been soaked in selenious acid.[1-4] Red amorphous selenium is precipitated when the gases pass through the filter, as shown in the following reaction:

$$H_2SeO_3 + H_2O + 2SO_2 \rightarrow Se + 2H_2SO_4$$

The filter medium is 0.5 m thick and the outer 0.3 m is impregnated with the precipitated selenium. The total filter area of about 100 m^2 is divided into two parallel units. The gas passes through the filter at a velocity of about 0.17 m/s, resulting in a contact time of 1 to 2 seconds.[1] Condensation of moisture on the filter must be avoided to prevent deactivating the selenium. The filter element can continue to absorb mercury until its content reaches 10 to 15 percent. At that time the filter is treated to recover mercury and regenerate the selenium.[1-4]

This type of selenium filter has been in operation for several years at Boliden's Rönnskär works and has effectively removed 90 percent of the mercury from a gas stream of 60,000 Nm^3/h flow rate containing 4 to 5 percent SO_2 and 0.85 mg/m^3 mercury. Occasionally, collection efficiencies of up to 99.9 percent have been achieved. Particulate mercury has been collected with approximately the same efficiency.[1]

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5.10 BOLIDEN WET SELENIUM SCRUBBING PROCESS

Boliden a.-b. has been using the wet selenium scrubbing technique since 1972 to remove mercury from roaster gases at its Helsingborg, Sweden, zinc facilities. The process utilizes amorphous solid selenium in suspension in a wet scrubber solution; the solution contains between 20 and 40 percent sulfuric acid. The acid concentration must be kept within these limits because complex and highly soluble selenium-sulfur compounds are formed at low H_2SO_4 concentrations. At high concentrations, the acid's oxidizing power becomes noticeable and selenium dioxide or selenite is formed.[1-4]

When the sulfide ore being roasted contains sufficient selenium, it may not be necessary to add more selenium to the scrubbing system; however, the activated selenium slurry must be recirculated at an adequate rate.[3]

Treatment of roaster gases containing 6 mg/m^3 mercury reportedly results in reduction of mercury concentrations to about 0.1 to 0.5 mg/m^3.

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3. Habashi, F. Metallurgical Plants: How Mercury Pollution Is Abated. Environmental Science and Technology, 12(13):1372-1376, December 1978.

4. Coleman, R.T., Jr. Emerging Technology in the Primary Copper Industry. Prepared for the U.S. Environmental Protection Agency under Contract No. 68-02-2608. Radian Corporation, Austin, Texas, August 1978.

5.11 BOLIDEN ACTIVATED CARBON PROCESS

The activated carbon process is used at Boliden's Rönnskär operation in Sweden. The process is based on the ability of activated carbon to adsorb 10 to 12 percent of its own weight in mercury vapor. Gas streams containing low levels of mercury (0.1 to 0.2 mg/m^3) are particularly well suited to application of this process.[1-4]

The Boliden unit consists of three towers connected in parallel, each with a capacity of 40,000 Nm^2/h of gas and containing 23 m^3 of activated carbon. During normal operation, mercury in the gas stream enters the filter at a rate of 10 g/h and leaves at 0.9 g/h, an efficiency of 90 percent. The gas input normally contains 3 to 6 percent SO_2, but the carbon is activated initially with a 100 percent SO_2 stream. For proper operation, the gas must be thoroughly dried and the temperature must not exceed 50°C.[1-4]

Initial cost of the Boliden unit in 1971 was about $210,000.[2]

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5.12 MERCURIC CHLORIDE SCRUBBING PROCESS[1]

Boliden a.-b. and Det Norske Zink Kompani have constructed a full-scale chloride scrubbing facility for removal of mercury from roaster gases at a plant in Eitrheim, Odda, Norway. The chloride scrubber is part of the gas cleaning system in an acid plant treating zinc roaster off-gases.

As illustrated in Figure 27, a chloride scrubber consists of a tower in which the chloride solution is sprayed downward, meeting a countercurrent flow of roaster gases; the tower is equipped with a mist eliminator, sludge separator, and recycle pump. Part of the wash solution is directly recycled and part is first treated in the sludge separator. Underflow is treated for mercury recovery.

Over a 2-year period, the process helped produce sulfuric acid with a mercury content of 0.5 ppm from the roasting of zinc concentrates with mercury levels of up to 150 ppm.

Initial cost of the scrubber, which was built in 1972-73, was about $310,000; operating costs have been estimated at less than 0.10/Mg of monohydrate. Power requirements for pumps and fans are 8 kWh/Mg of sulfuric acid.

Reference

1. Sundstrom, O. Mercury in Sulphuric Acid: Boliden Processes Can Control Hg Levels During or After Manufacture. Sulphur No. 116:37-43, The British Sulphur Corp., January-February 1975.

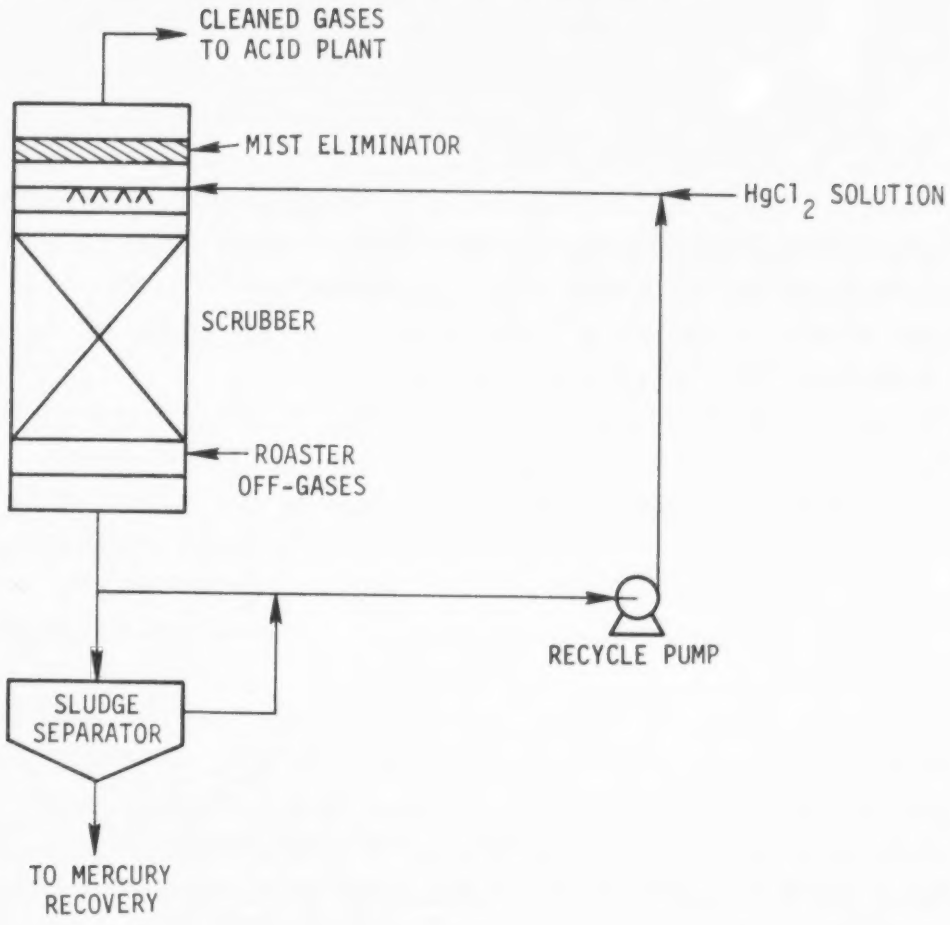

Figure 27. Mercuric chloride scrubbing process.[1]

5.13 OUTOKUMPU SULFURIC ACID SCRUBBING PROCESS

The Outokumpu process was developed to remove mercury from SO_2-laden roaster gases at the Kokkola electrolytic zinc plant; the process began operation in 1970. The same process has been used in Japan at the Onahama plant of Toho Zinc Co. and the Miike smelter of Mitsui Mining and Smelting Co., Ltd.[1,2]

At Kokkola, the gas from the fluidized bed roaster contains 9 to 11 percent SO_2 at 950°C. After the gas passes through a waste heat boiler and a series of electrostatic precipitators and cyclones, the temperature drops to about 350°C. Gas leaving the electrostatic precipitators contains about 40 to 80 mg Hg/m^3 and, as shown in Figure 28, enters a sulfatizer, which consists of a brick-lined tower packed with ceramic shapes. In the sulfatizer, the gas contacts a countercurrent flow of concentrated (over 80 percent) sulfuric acid. Selenium and mercury are scrubbed from the gas along with any zinc or iron present.[1,2]

The temperature of the gas is controlled by an external heat exchanger and by the rate of acid circulation to prevent dilution of the sulfuric acid by moisture in the gas. Thus, the vapor pressure of the water in the acid corresponds to the water partial pressure of the gas. At Kokkola, the acid inlet and outlet temperatures are 40° and 180°C.[1,2]

The metal containing acid flows from the tower bottom to a strong tank, from which a portion is pumped through a heat exchanger and returned to the tower. Another portion is routed to a clarifier for removal of the mercury, selenium, and zinc.[1,2]

Gas exits the sulfatizer at 180°C with about 0.2 mg elemental mercury/Nm^3 and is then washed with weak (about 30 percent) sulfuric acid in the normal scrubber of the sulfuric acid plant. The temperature is decreased to about 60° to 70°C, and the chloride content is reduced to a level suitable for sulfuric acid production. The gas is tested in an electrostatic precipitator before being routed to the acid plant.[1,2]

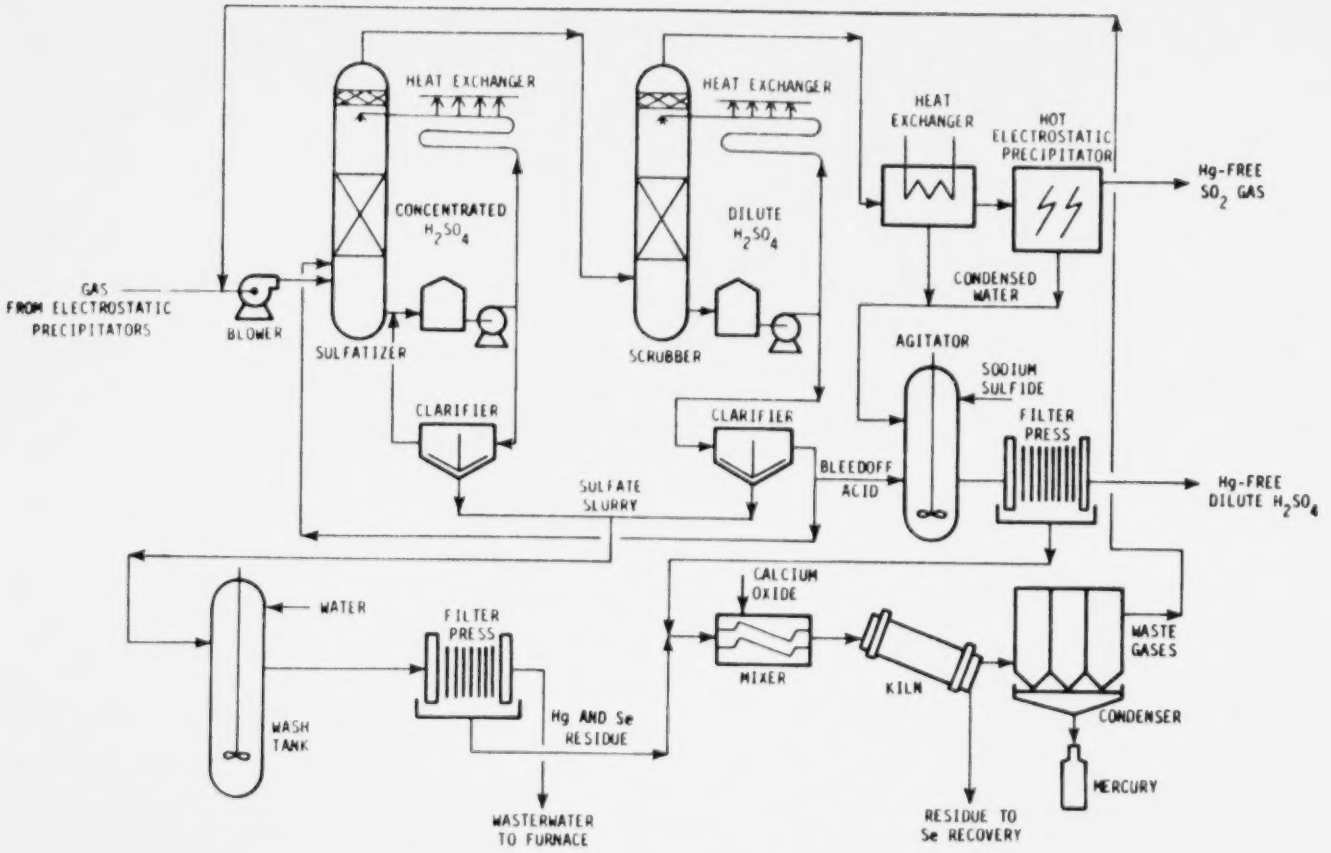

Figure 28. Outokumpu sulfuric acid scrubbing process.[2]

Concentrated acid carryover, residual mercury, and selenium are removed in this weak scrub. These materials are separated from the weak acid in the clarifier, and the underflow is combined with the underflow from the sulfatizer's clarifier. The clarifier overflow is used to make up concentrated acid loss and is returned to the sulfatizer.[1,2]

Precipitates from underflow of the two clarifiers are washed with water to dissolve the sulfuric acid, iron, and zinc salts; the residue contains about 50 percent insoluble mercury and 10 percent selenium compounds. Washwater is fed to the roasting furnace to ensure complete metal recovery, and the residue is mixed with a fixed proportion of lime and fed to a kiln, where it is heated to 650° to 700°C. The mercury compounds decompose, and mercury vaporizes, exits the kiln, and is recovered in a condenser. Sulfur and selenium combine with the lime to form stable compounds; this material serves as feedstock for production of metallic selenium. Gas from the kiln, which contains mercury not recovered in the condenser, is combined with roaster gases ahead of the sulfatizer.[1,2]

The Outokumpu process is working successfully with concentrates containing up to 250 ppm mercury. The cleaned gas stream entering the acid plant usually contains between 0.1 and 0.2 mg mercury/Nm^3, and the product acid contains less than 1 mg mercury/liter.

One disadvantage of the Outokumpu process is that the high temperatures involved can cause corrosion. Another disadvantage is that the dust removed by the hot electrostatic precipitator preceding the sulfatizer can scatter and react with the acid to produce other sulfates, which may deposit within the pipes when the acid is cooled.

The installed cost of the sulfatizer and associated equipment is between $13 and $16 per annual megagram of sulfuric acid capacity. Retrofit of a facility such as this is more expensive. The most significant operating cost appears to be maintenance, which is about 10 percent of the yearly capital costs.[1]

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5.14 CENTRO NACIONAL DE INVESTIGACIONES PROCESS[1]

Centro Nacional de Investigaciones (CENIM) in Spain has developed a process for the removal of mercury from the stack gases at its Almaden mercury plant.

Mercury ore is heated on rotary kilns to volatilize mercury:

$$HgS + O_2 \rightarrow Hg + SO_2$$

The gas is cooled, and the mercury is condensed; gases leaving the condenser contain about 70 ppm mercury. The gases are washed with sodium thiocyanate to reclaim this mercury. About two-thirds of the mercury is dissolved as the sodium thiocyanate complex, and one-third precipitates as mercuric sulfide as indicated below:

$$3Hg + 8NaSCN + 2H_2SO_4 + SO_2 \rightarrow 2Na_2[Na(SCN)_4] + HgS + 2Na_2SO_4 + 2H_2O$$

Sodium sulfate is added to the solution to achieve complete precipitation of mercury as HgS and concurrently to regenerate the sodium thiocyanate solution:

$$Na_2[Hg(SCN)_4] + Na_2S \rightarrow + 4NaSCN$$

The HgS is filtered out, and the solution is recycled; however, the formation of sodium sulfate eventually reaches the point where it crystallizes and contaminates the HgS. The sodium thiocyanate and sodium sulfate are separated by fractional crystallization to avoid this problem.

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1. Habashi, F. Metallurgical Plants: How Mercury Pollution is Abated. Environmental Science and Technology, 12(13):1372-1376, December 1978.

5.15 DEMARC D PROCESS[1,2]

Showa Denko K.K. of Japan has developed the DeMarc D process for removal of mercury from smelter gases containing sulfur dioxide. Three Japanese smelters treating copper and zinc concentrates have piloted this patented process.

Smelter gases are cleaned in a boiler/electrostatic precipitator system and are then cooled to 130° to 150°C; they are next passed through towers packed with activated carbon. The carbon is impregnated with an inexpensive reagent. Steam is used to regenerate the carbon and recover the mercury.[1,2]

The pilot systems have reportedly operated successfully on gas streams containing 8 percent SO_2 and 5 mg mercury/Nm^3. Over 99 percent of the mercury is removed from the gas, and the product sulfuric acid contains less than 0.1 ppm mercury.

The capital cost of a pilot-scale facility (50,000 m^3/h) in 1976 was reported as $520,000, and the estimated direct operating cost for a gas containing 5 mg mercury/m^3 is $2/Mg acid. Energy consumption for 1000 m^3 of gas is 2.26 liters of fuel oil and 6.7 kWh of electricity. Smelters with large gas volumes can experience difficulties with the DeMarc D process. Use of a filter technique can be expensive, and a large amount of gas cooling is required.

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5.16 BOLIDEN PROCESS[1]

The process developed by Boliden a.-b. of Sweden for removal of mercury from sulfuric acid involves the addition of sulfur as sodium thiosulfate to the acid. The sodium thiosulfate decomposes to form elemental sulfur in a fine colloidal form and oxides of mercury. This process is only applicable to acid of 85 percent strength or less because higher concentrations oxidize the sulfur to sulfur dioxide.

A dosage of 0.5 kg of sodium thiosulfate per cubic meter of cooled, diluted acid is enough to reduce the mercury content from 15 ppm to less than 0.5 ppm in about 1 hour, after which the acid is filter-pressed.

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5.17 MITSUI PROCESS[1,2]

Mitsui Mining and Smelting Co. uses powdered aluminum to remove mercury from sulfuric acid produced at a lead-zinc smelter in Kamioka, Japan. In addition, Akita Zinc, Ltd., reportedly uses the Mitsui process at an electrolytic zinc plant in Iijima, Japan.

The process involves adding powdered aluminum to acid and allowing 24 hours for a reaction in water-cooled vessels. The acid solution is then pressure-filtered to produce sulfuric acid containing about 5 ppm mercury and a filter cake of about 10 percent mercury. The filter cake can also contain selenium, lead, and other impurities.

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5.18 GORTDRUM MINES PROCESS

Gortdrum Mines, Ltd., of Ireland has developed an unusual technique for the treatment of mercury-laden copper concentrates. The technique is applied to copper-arsenic-antimony sulfide concentrates containing 0.05 to 0.9 percent mercury before shipment to a smelter.[1,2]

As shown in Figure 29, the concentrate is fed to a multiple-hearth roaster, where it is heated in a neutral atmosphere (1 to 2 percent O_2) to a temperature of 650°C at the final hearth.

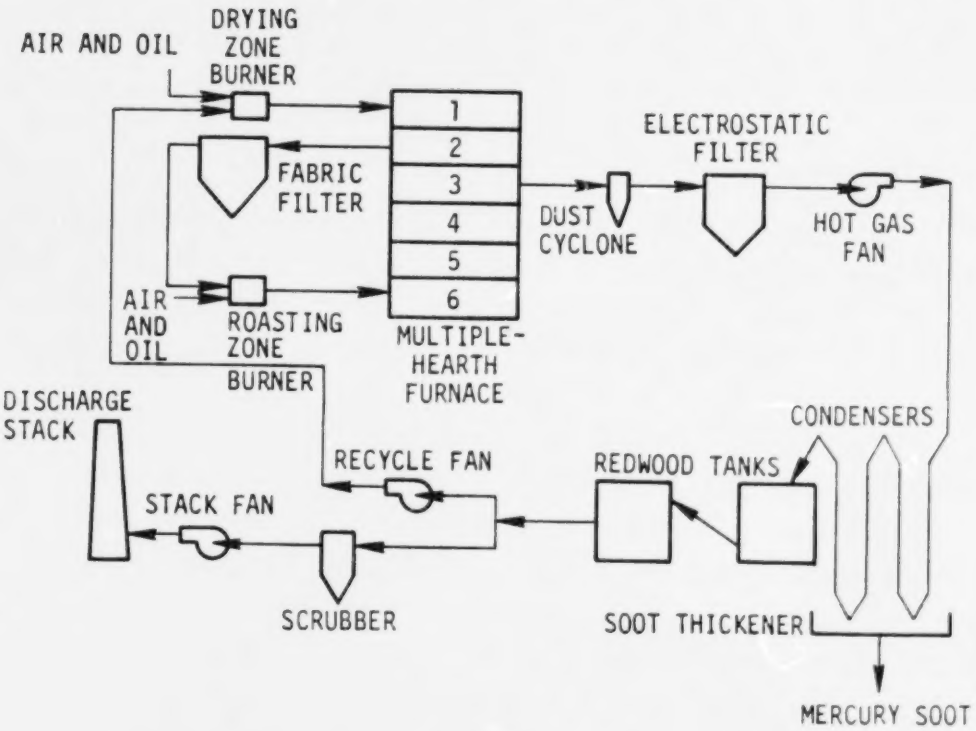

Figure 29. Flowsheet of solids for Gortdrum Mines process.[2]

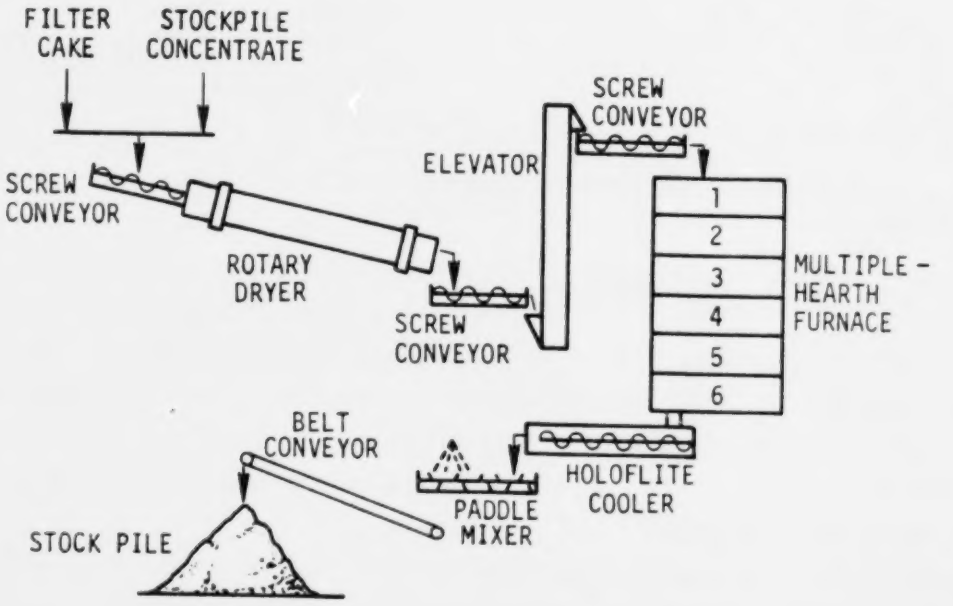

Figure 30. Flowsheet of gases for Gortdrum Mines process.[2]

Oxygen content is limited to minimize physical and chemical changes in the concentrate and inhibit formation of sulfur dioxide and arsenic and antimony trioxides. Approximately 90 percent of the mercury is volatilized in the roaster; this mercury is removed from the roaster off-gas by cooling the gas from 160° to 22°C in water spray condensers. The condensate, which contains about 50 percent mercury and 2 percent copper, is collected in a water seal and treated for recovery of the mercury. Figure 30 shows the final wet scrubber, which follows the condenser and cleans the gas of any remaining condensed mercury before discharge to the atmosphere. Mercury concentration in the tail gas has not been reported.[1]

Because this process is operated as a separate facility, the capital and operating costs should be high. A unit capable of treating 12,000 Mg/yr of concentrate was estimated to cost over $2,000,000 (Canadian) in 1976.[1] Operating costs in 1972 were given as $23.87(Canadian)/Mg; fuel oil and electricity accounted for about 17 percent ($4.02) of this amount.[2]

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5.19 SWINGAWAY CONVERTER HOODS[1-3]

Peirce-Smith converters are a major source of fugitive emissions at primary copper smelters. Various types of collection systems are used, either singly or in combination, to control some of these emissions.

Nippon Mining Company of Japan uses a swingaway hood with a retractable secondary hood above. During a blister copper pour, emissions are deflected into the secondary retractable hood.

Emissions entering the hooding system are then routed to a collection system. During blowing, slagging, and pouring of blister copper, this system can be very efficient.

The swingaway hood can be a steel shell with a castable refractory lining, pillar mounting, and motorized mechanism. In the retracted position, a swingaway hood must be clear of the converter aisle and slightly behind the converter to eliminate interference with the crane.

References

1. Niimura, M., et al. Control of Emissions at Onahama Copper Smelter. Presented at the Joint Meeting of the Mining and Metallurgical Institute of Japan and the American Institute of Mining, Metallurgical, and Petroleum Engineers, Tokyo, Japan, May 24-27, 1972.

2. Sharma, S.N., et al. Control of Secondary Emissions From Copper Converters in Copper and Nickel Converters. In: AIME Symposium Proceedings, New Orleans, Louisiana, February 19-21, 1979. pp. 312-335.

3. PEDCo Environmental, Inc. Pollution Control in the Japanese Primary Nonferrous Metals Industry. Prepared for the U.S. Environmental Protection Agency under Contract No. 68-02-1375, Task No. 36. Cincinnati, Ohio, March 1978.

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5.20 ACCORDION DOOR SECONDARY HOODING[1-3]

Accordion door secondary hooding for copper converters is in use at the Onahama Smelting and Refining Co., Ltd., Onahama, Japan. This involves placing a completely enclosed hood over the primary hood, as shown in Figure 31. During blowing and non-blowing, fugitive gases are collected through a separate duct-fan system, cleaned in a wet ESP, and discharged through a 75-meter stack.

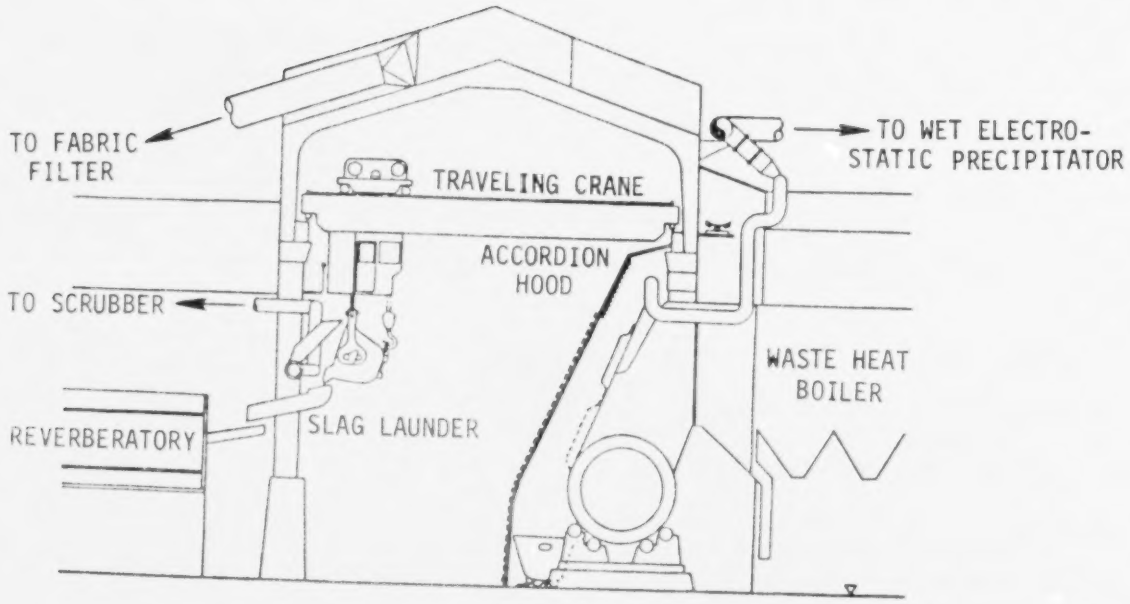

Figure 31. Accordion door secondary hooding at Onahama.[3]

The converter building at Onahama is completely sealed, and the ventilation air and gas escaping the secondary hoods are drawn out by a fan and routed through a fabric filter before discharge.

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1. Niimura, M., et al. Control of Emissions at Onahama Copper Smelter. Presented at the Joint Meeting of the Mining and Metallurgical Institute of Japan and the American Institute of Mining, Metallurgical, and Petroleum Engineers, Tokyo, Japan, May 24-27, 1972.

2. Sharma, S.N., et al. Control of Secondary Emissions from Copper Converters in Copper and Nickel Converters. In: AIME Symposium Proceedings, New Orleans, Louisiana, February 19-21, 1979. pp. 312-335.

3. PEDCo Environmental, Inc. Pollution Control in the Japanese Primary Nonferrous Metals Industry. Prepared for the U.S. Environmental Protection Agency under Contract No. 68-02-1375, Task No. 36. Cincinnati, Ohio, March 1978.

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5.21 ENCLOSED TWO-POSITION SECONDARY HOODING[1]

Boliden a.-b. of Sweden uses an enclosed, two-position gate design in its secondary hooding of copper converters. As shown in Figure 32, this secondary hood is located over the front of the primary hood and supports a trackway for a single rolling door that covers only 50 percent of the hood opening. One-half of the hood is always open to capture fugitive gas.

The rolling door must be down for charging and up to allow access to the ladle, but at other times the door position, and thus the ventilated zone, is adjustable at the discretion of the

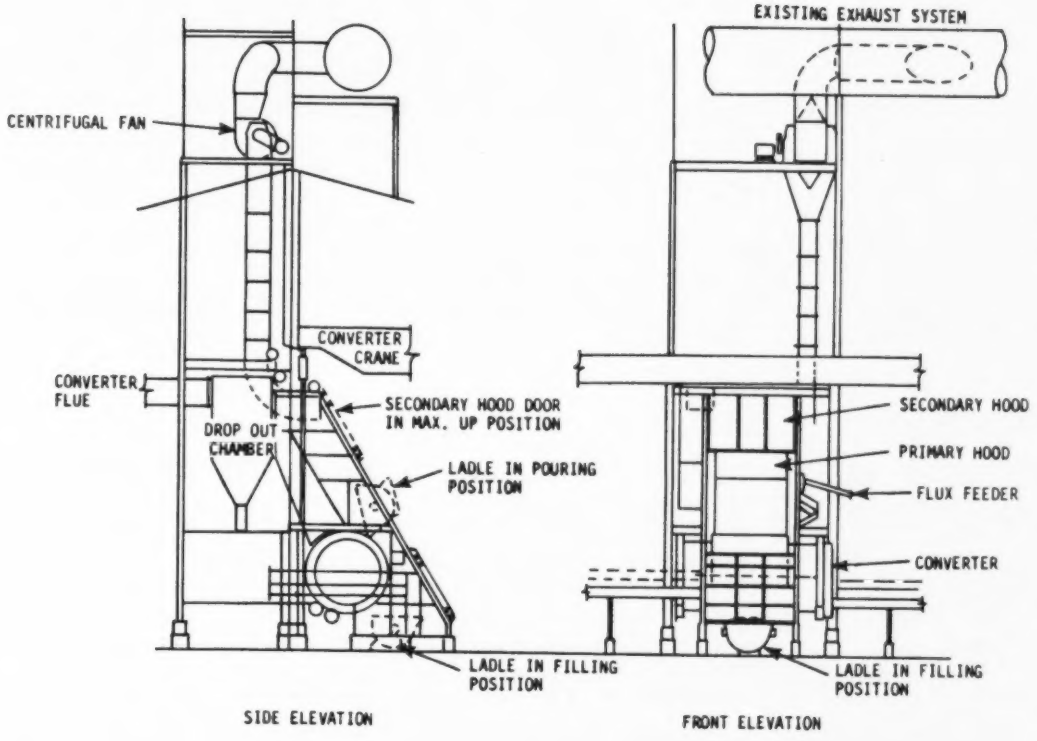

Figure 32. Enclosed two-position secondary hooding.[1]

converter operator. Access to the converter for observation, sampling, cleaning, and repairing is provided by openings in the sides of the secondary hood.

The secondary hood, which is about 34 m^2 in area, clears the whole primary hood door mechanism and cooling system. The exhaust system operates continuously.

Reference

1. Sharma, S.N., et al. Control of Secondary Emissions From Copper Converters in Copper and Nickel Converters. In: AIME Symposium Proceedings, New Orleans, Louisiana, February 19-21, 1979. pp. 312-335.

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5.22 AIR CURTAIN HOODING[1]

Mitsubishi Metal Corporation uses primary and secondary hooding in conjunction with an air curtain to control fugitive emissions from Peirce-Smith converters at its primary copper smelter in Onahama, Japan.

The primary hoods fit tightly on each converter (with a gap of only 5 to 8 cm), almost completely capturing emissions during the blowing cycle. During charging and pouring the primary hood draft is reduced by about 65 to 80 percent, capturing about 30 to 50 percent of fugitive emissions. Control of the remainder of the fugitives is provided by the secondary hoods, air curtains, and building exhaust ventilation.

The secondary hoods are sheet metal panels on either side of the converter that rise about 14 meters from the floor. At the top of these panels, three fans are fitted into the hood, creating an air curtain across the slot in the top of the hood. The slot is large enough to allow crane cables to maneuver during

charging and pouring. On the other side of the slot is a duct that collects the exhaust from the three air curtain fans. The exhaust duct for the secondary hood is atop the panels on the side farthest from the aisle. Figure 33 shows this configuration. The secondary hood operates all the time; it has been observed to capture an estimated 30 to 50 percent of the gases escaping the primary hood during charging and pouring, and nearly all fugitives during blowing and standby.

The unique feature of this system, however, is the air curtain across the slot in the secondary hood. Three fans create the stream of air that passes above the slot and enters the capture duct on the opposite side of the slot. This "push/pull" technique is extremely effective in collecting fugitive gases that would normally escape through the slot. The gases collected by the air curtain contain 100 to 200 ppm SO_2; they are sent through a fabric filter prior to discharge through a stack.

Reference

1. Coleman, R.T. Trip Report: Mitsubishi Metals Corporation, Onahama, Japan, July 9-10, 1979. Radian Corporation, Austin, Texas, 1979.

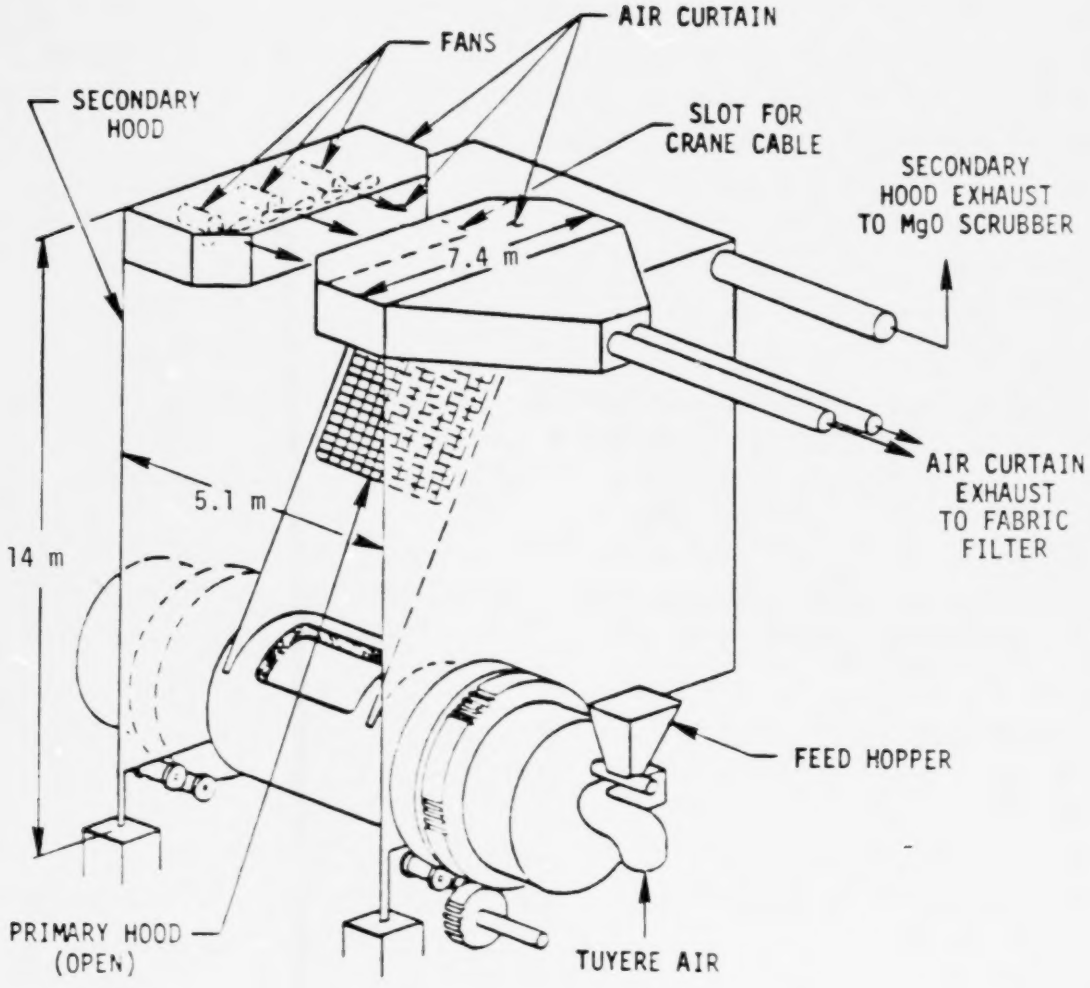

Figure 33. Air curtain hooding.[1]

SECTION 6

WATER POLLUTION CONTROL PROCESSES

6.1 BOLIDEN SULFIDE PRECIPITATION PROCESS

Boliden a.-b. of Sweden has recently installed a wastewater treatment facility at its Rönnskär works that makes use of sulfide precipitation for control of heavy metals. This new facility treats both process waters and plant runoff from the primary copper and lead smelter.[1,2]

The Rönnskär plant is designed to handle an average wastewater flow of about 200 m^3/h. A flow diagram for the plant is presented in Figure 34. Process water with a pH of approximately 2.0 enters the plant and is treated with sodium hydroxide to raise the pH to about 3.0. This initial pH adjustment helps prevent corrosion of the equipment. Pretreatment of runoff consists of equalization and grit removal. Following pretreatment, the process and runoff streams are combined for subsequent treatment in a series of three flash-mix reactors.[3]

The first reactor has a capacity of 50 m^3 and an average residence time (RT) of about 15 minutes. Sodium hydroxide is added to the wastewater in this reactor. A pH of 4.0 to 5.0 is attained; this pH range appears to be optimum for sulfide precipitation.[3]

The second reactor has a capacity of 30 m^3 with an average residence time of about 9 minutes; sodium sulfide is added to the stream. The third reactor is auxiliary to the second, providing additional residence time for treatment with sodium sulfide if required. The addition of the sodium sulfide produces the following reactions.[3]

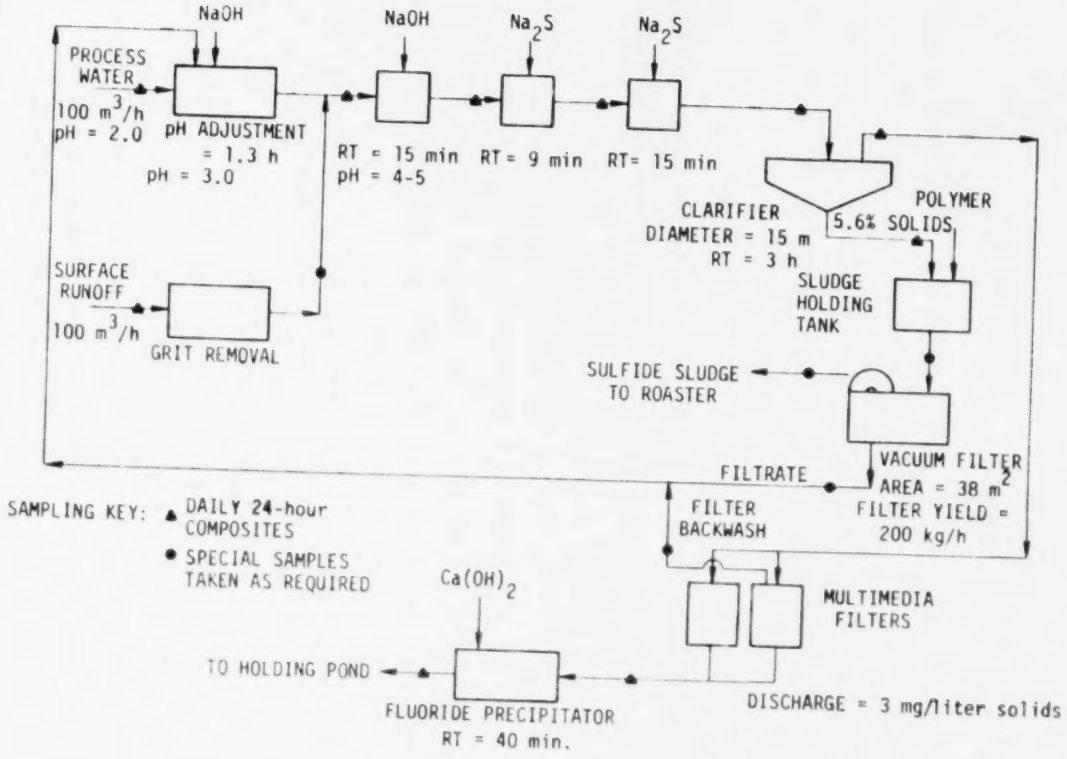

Figure 34. Simplified flowsheet of the Boliden sulfide precipitation process.[3]

$$Na_2S \rightleftharpoons Na^+ + S = M^{++} + S = \rightleftharpoons MS\downarrow$$

The dissolved metal cations form metal sulfide precipitates. Excess sulfide must be avoided to eliminate the potential formation of hydrogen sulfide.[3]

Clarification and sludge thickening are accomplished in a circular clarifier having a diameter of 15 m and an average flow rate of 200 m^3/h; detention time is about 3 hours. The clarifier is equipped to feed polymer coagulants to the stream.[3]

Overflow from the clarifier has been estimated to contain less than 50 mg/liter of solids, and bench-scale tests by Boliden indicate that levels as low as 15 mg/liter may be possible. Two trimedia filters, however, are utilized at the plant to achieve a level of 3 mg/liter solids. The filters are each 3 m in diameter and 1.3 m deep; they are reportedly backwashed every 24 hours, with the backwash returned to the pH adjustment tanks.[3]

Sludge from the clarifier has been estimated to contain 5 to 6 percent solids; it is first routed to a holding tank where a polymer is added to aid in subsequent dewatering. Dewatering is accomplished in a vacuum filter operating 8 to 10 hours per day, 7 days per week. The filter has a fabric area of 38 m^2 and produces an estimated 200 kg dry solids per hour of sludge with a solids content of 25 percent. This sludge is charged to the copper roasters and the filtrate is returned to the pH adjustment tanks.[3]

The process water initially contains a relatively high concentration of fluorides, and evaporation during processing results in an even higher level. Consequently, a separate unit is installed in the wastewater treatment plant for the control of fluorides. This unit consists of a flash mix/flocculator to which hydrated lime is added.[3]

Domestic research into the effectiveness of sulfide precipitation indicates its apparent superiority to conventional hydroxide (lime) precipitation in the removal of heavy metals from both synthetic mixtures and actual scrubber waste from a copper smelting operation.[4]

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1. Coleman, R.T., et al. Test Program for Characterizing Boliden Aktiebolag's Sodium Sulfide Precipitation Process. Prepared for U.S. Environmental Protection Agency under Contract No. 38-02-2608. Radian Corporation, Austin, Texas, March 6, 1978.

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Schlauch, R.M., et al. Treatment of Metal Finishing Wastes by Sulfide Precipitation. EPA 600/2-77-049, February 1977.

6.2 FERRITE PRECIPITATION PROCESS[1]

Fuji Kasui Engineering Co., Ltd., of Japan, has developed a process for removing heavy metals from wastewater by converting them to ferrite precipitates (patent).

In this process, as shown in Figure 35, iron compounds such as ferrous sulfate are used as precipitating agents in quantities that depend upon the type of metal to be removed. For example, experimental work indicates that zinc, manganese, and copper can

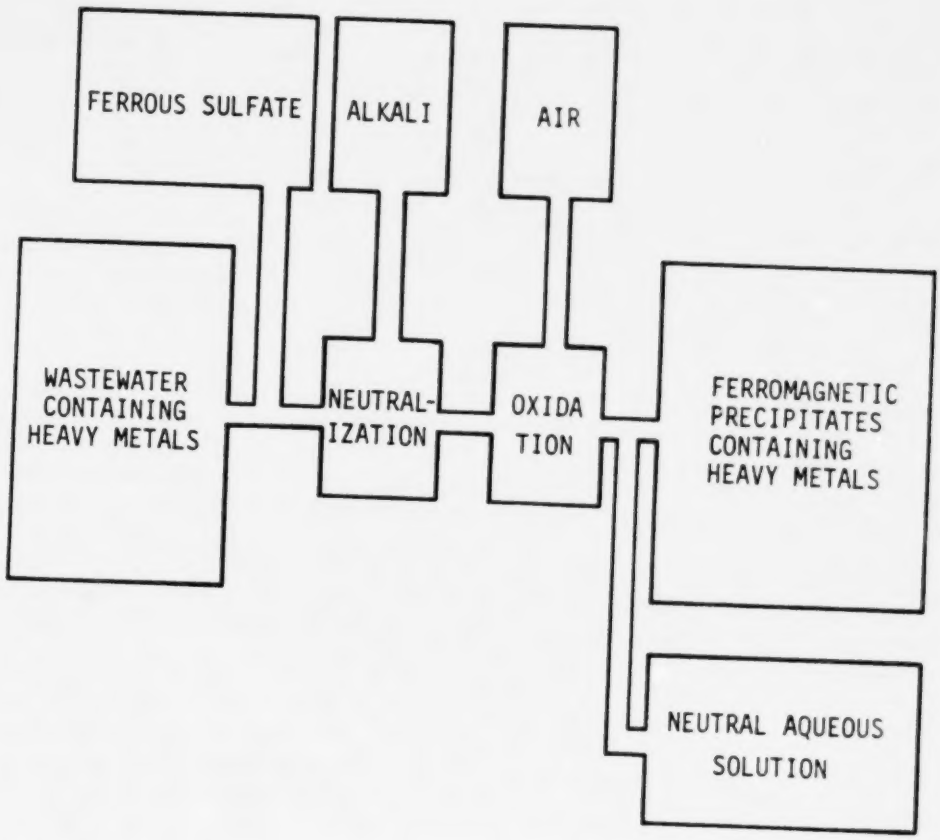

Figure 35. Ferrite precipitation process.[1]

easily be converted to ferrite. The addition of ferrous salt in a quantity twice the molar ratio of those metals is sufficient to accomplish this conversion. Metals such as tin and lead, however, do not easily form solid ferrites; they require the addition of large quantities of ferrous salt.

Posttreatment metal concentrations in the aqueous solutions used in experimental trials of the ferrite precipitation process were significantly lowered: for example, copper from 9500 ppm to 0.5 ppm and cadmium from 1800 ppm to 0.1 ppm. The heavy metal ions were converted to ferrite precipitates and separated magnetically.

This process has several advantages, which are described below, over conventional techniques.

Precipitates formed by conventional processes may redissolve after disposal; those formed by this new process have very little risk of redissolution.

Precipitates formed by conventional processes are so fine that they cannot be filtered, while precipitates formed by the ferrite process have an average particle size suitable for filtration. In addition, they can be separated and removed magnetically because they are ferromagnetic materials.

Iron compounds used in this process, such as ferrous sulfate, can be obtained in large quantities as industrial wastes.

The most suitable condition for precipitation in conventional processes varies according to the type of heavy metal. Consequently, each heavy metal must be treated individually. In the ferrite process, wastewaters that contain various types of heavy metals can be treated at the same time once the most suitable condition for precipitating ferrite is established.

Unlike conventional processes, this one can remove hexavalent chromium ions Cr (VI). This occurs by reduction of the hexavalent chromium ions followed by precipitation.[1]

Reference

1. U.S. Patent Office. Ferrite Process: New Technology for Removing Heavy Metals from Wastewaters. Patent No. 3,822,210 issued to Fuji Engineering Company, Ltd.